THE SELECTION, INTEGRATION, AND EVALUATION OF A PAYLOAD FOR CHEMICAL PLUME DETECTION ON AN AUTONOMOUS UNDERWATER VEHICLE

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The Selection, Integration, and Evaluation of a Payload for Chemical Plume Detection on an Autonomous Underwater Vehicle

By
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ABSTRACT

The oil and gas industry is growing off the East Coast of Canada, and as a result the discharges associated with production continue to grow. Mandates are in place to ensure that these activities proceed in an environmentally acceptable manner. Policies are being introduced worldwide that are leading to zero-discharge or the use of complex risk assessment processes to determine the environmental impacts of these discharges. Little real data exists about the environmental effects of these discharges, and new and innovative methods for data collection need to be considered. One possibility is to use autonomous underwater vehicles (AUV) for environmental monitoring, which is explored in this thesis.

The steps associated with choosing and implementing an environmental payload on an AUV are discussed in this thesis. It was determined that sample collection methods were not appropriate for use on an AUV, but that in-situ sensors were useful for collecting environmental data. Sea-trials were performed in Burrard Inlet, British Columbia between February 4 and February 6, 2002. The AUV used for this project was the ARCS vehicle, supplied by International Submarine Engineering in British Columbia. The payload for this mission used two in-situ instruments, which were supplied by Applied Microsystems Ltd. The first was an underwater mass spectrometer called the "In-Spectr". It is capable of measuring dissolved gases and volatile organic chemicals to atomic masses of up to 200 atomic mass units. It was used in a continuous mode of sampling that indicated the presence or absence of a chemical. The second instrument measured

conductivity, temperature, and depth (CTD) and was called the "Micro-CTD". These instruments were user-friendly and easily integrated into the ARCS vehicle.

The trials were successful in demonstrating the use of an underwater mass spectrometer on an AUV. It was shown that the payload could be used to detect chemical plumes, which might be considered a viable option for environmental monitoring offshore. A chemical tracer, dimethyl sulphide (DMS), was pumped into the water at a maximum rate of 9 L/h, as stipulated by the BC Ministry of Water, Land and Air Protection. The mass spectrometer successfully detected the location of the DMS in the water ±13.5 m. The CTD was used to complement this data. Temperatures in the Inlet were relatively constant, with variations within one degree Celsius. Salinity increased with depth. The fresher water on the surface could be attributed to the larger volumes of precipitation during the winter months in that geographic region.

The mass spectrometer was highly sensitive to power interruptions, which forced the instrument to shutdown. It was recommended that a back-up power system be provided. It was also recommended that the internal clocks on all instruments be synchronized before the sea-trials to simplify data analysis.

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CHAPTER 1 INTRODUCTION AND BACKGROUND

1.1 INTRODUCTION

1.1.1 PROBLEM STATEMENT

Offshore oil and gas production worldwide is facing the introduction of policies leading to zero discharge or a complex risk assessment process to determine environmental impacts. In the interim, discharges on the East Coast of Canada will continue to grow with continuing development of the oil and gas industry. The regulating bodies for offshore oil production, such as the Canadian-Newfoundland Offshore Petroleum Board, have a mandate to ensure that offshore oil and gas activities proceed in an environmentally acceptable manner (CNOPB, 2002). For these reasons, environmental effects monitoring associated with offshore oil and gas requires continual development.

At present, monitoring typically involves periodic sample collection techniques deployed from a ship. These methods are usually expensive and incomplete, giving only a small amount of information, as they cannot account for the dynamic ocean environment and changes in discharges with time. Due to the methods of sampling, there is an increased likelihood of sample contamination and chemical degradation. Numerical models often attempt to simulate effluent discharges, but they lack real data for calibration and validation (Mukhtasor, 2001). Required data for detailed risk analysis is also lacking (Sadiq, 2002). New and innovative means of acquiring information need to be considered.

The work of this project is part of a larger project entitled "Offshore Environmental Research Engineering Using Autonomous Underwater Vehicles" (OERE/AUV). The overall project is funded through a Strategic Project provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) with support from the following partners: Memorial University of Newfoundland (MUN); National Research Council (NRC) of Canada's Institute for Marine Dynamics (IMD); Centre for Cold Ocean Research Engineering (C-CORE); University of Victoria; Petro Canada as Operator of the Terra Nova Project; International Submarine Engineering (ISE); and Geo-Resources Inc.

The work focuses mainly on the impacts of offshore discharges such as produced water, drilling muds, and rock cuttings on the surrounding ocean environment. There are three main goals of the OERE/AUV project. They are:

1. To develop and use improved numerical models to assess and manage the impacts of discharges of produced water, rock cuttings, and drilling muds from offshore oil and gas operations on the East Coast of Canada;
2. To assess new technologies and compare them with existing methods and benchmarks aimed at reducing the impact of pollutants and toxicants from produced water, rock cuttings and drilling mud discharges from offshore operations; and
3. To develop autonomous underwater vehicles (AUVs) for use as remote sensing tools to further the understanding of human activities in environmental processes in the offshore oil and gas industry.

The work started in January 2000 and is set to take place over a five-year period. The overall project is being managed by Dr. Neil Bose.

1.1.2 Objectives and Goals

The overall objective of this thesis project was to investigate the use of autonomous underwater vehicle technology to obtain environmental information about produced water discharges.

The primary goal of this project was to develop and test a payload on an autonomous underwater vehicle that can be used to perform environmental discharge monitoring. Alternative methods of gaining environmental data were examined: sampling and in-situ sensors. Another objective was to assess the potential of this payload to be deployed to monitor produced water discharges.

1.1.3 THESIS OVERVIEW

Chapter 1 introduces the project and its role in the overall research project with several partners. The long-term and immediate goals are discussed and background information on the subjects relevant to the project is provided. The subsequent chapters discuss the use of chemical tracers in the field, the experimentation procedure (including a detailed description of all equipment used), a detailed discussion of the results, and the conclusions and recommendations.

1.2 BACKGROUND

This work was driven by a number of factors including the growing offshore industry on the East Coast of Newfoundland, the lack of knowledge of the toxicity and potential effects of produced water, the use of AUV technology for environmental monitoring, and the development of an underwater mass spectrometer. Due to the wide variety of elements, this section has been broken down into subsections to give background information on each particular element.

1.2.1 North Atlantic Offshore Oil and Gas Developments

The East Coast of Canada, including offshore Newfoundland, has recently been considered to be a major new territory of offshore oil and gas production. The main focus of Newfoundland and Labrador petroleum exploration has been the basins off the East Coast, however, during the last decade, exploration has occurred off of the West Coast as well (Government of Newfoundland and Labrador, Department of Mines and Energy, Energy Branch, 2000). As of May 2000, 125 exploration wells, 31 delineation wells and 27 development wells have been drilled offshore of the province. Recoverable resources of 2.1 billion barrels of oil, 9.3 trillion cubic feet of natural gas and 413 million barrels of natural gas liquids have been estimated (Government of Newfoundland and Labrador, Department of Mines and Energy, Energy Branch, 2000). All of the major oil discoveries have been in the Jeanne d'Arc Basin, which covers about 14,000 square kilometers off the East Coast of Newfoundland. This includes developments such as Hibernia, Terra Nova, and White Rose. Hibernia and Terra Nova produced a combined average of about 240 000 barrels of oil per day in 2002 and first oil is expected at White Rose near 2005 (CNOPB, 2002).

1.2.2 Produced Water

Produced water is the largest waste stream generated in the production phase of offshore oil and gas operations. It is a complex mixture of inorganic and organic compounds. Models of the effluent fate predict that produced water will be rapidly diluted and dispersed when discharged into the ocean, however, little real data exists (Anderson, Rivkin and Warren, 2000).

Produced water discharges can have very large flow rates. In the North Sea, a typical discharge rate for produced water for a typical platform could be 10 000 m^3 per hour. The volume of produced water over the life of the development can be substantial. Over the economic life of the producing field, the quantity of discharge can be typically 10 times as high as the volume of the hydrocarbon produced (Stephenson, 1992).

Produced water has the potential to be toxic to the ocean environment. Constituents of concern contained in produced water include hydrolysis metals, heavy metals, petroleum hydrocarbons, nutrients, radionuclides and treatment chemicals (Lee et al., 2000). Samples of produced water collected from a well on the Scotian Shelf on the East Coast of Canada showed elevated concentrations of aluminum, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc, as well as hydrocarbons. In the same study, Microtox® assay results indicated an increase in produced water toxicity with time (Lee et al., 2000). This may be due to such factors as bioavailability, or chemical reactions that may take place over time. This author suggested that the chronic effects might be more significant than acute effects in produced water discharges. Mukhtasor (2001) suggested that the ecological risk assessment of produced water should be taken into consideration when designing production platforms. Reasons such as these, coupled with the lack of information indicate that new and innovative methods of investigating and monitoring produced water must be considered.

1.2.3 AUV TECHNOLOGY

Autonomous underwater vehicles (AUVs) are self-propelled underwater vehicles that perform a pre-determined mission completely unmanned (Curtis, 2001). They have moved from a state of research and development, and are beginning to receive commercial acceptance (Wernli, 2000). Examples of past uses are the laying of underwater cables and the operation of side-scan sonar for geo-physical and ocean bed surveys. As an AUV needs no crew, it could be miles from any support vessel or shore for hours at a time (Curtis, 2001). AUV technology is developing rapidly, and has the potential to be used in environmental monitoring.

1.2.4 ARCS VEHICLE

For this project, the ARCS vehicle was used. ARCS is an existing AUV developed by ISE Research Ltd. as a platform for underwater vehicle research for the Canadian Department of National Defence and the Canadian Hydrographic Service in the mid-1980s. The development and testing of ARCS took place between 1983 and 1986. Since 1987 the vehicle has been used for development and demonstration of AUV technologies including mission controllers, navigation systems, ballast and trimming systems, and advanced power sources. Over 800 successful dives have been conducted (ISE, 2002). Table 1-1 lists the specifications of ARCS as it presently exists.

Table 1-1: ARCS Specifications

Length	6.4 m / 21 feet
Diameter:	68.6 cm / 27 inches
Displacement:	1360.8 kg / 3000 lb
Speed:	4 knots; 5.5 knots (top)
Range:	36 km / 22.5 Nm with single NiCd battery 72 km / 45 Nm with double NiCd battery 235 km / 125 Nm with aluminium oxide fuel cell
Depth:	304.8 m / 1000 feet
Propulsion:	2.5 HP brushless DC motor
Power:	One or two 10 kWh Nickel Cadmium batteries 100 kWh Aluminium Oxygen fuel cell
Supervisory Control:	Triple diverse full duplex acoustic telemetry link (FSK)
On-board Control:	Motorola 32-bit processor with real time proprietary control system
Navigation Sensors:	Honeywell 726 MAPS inertial navigation unit EDO 3050 Doppler Sonar Strain gauge depth transducer
Navigational Accuracy:	<1% of distance travelled
Obstacle Avoidance:	ISE Mesotech 200 kHz obstacle avoidance sonar

1.2.5 Underwater Mass Spectrometer

Researchers at the Center for Ocean Technology at the University of South Florida have developed an underwater mass spectrometer (Short et al., 2000). This type of technology provides the opportunity to perform chemical analysis *in situ*. Traditionally, ocean samples have been collected and returned to land-based laboratories for analysis. Such sampling poses limitations on the frequency and analysis of sampling from dynamic environments. In addition, the likelihood of sample contamination and chemical degradation is relatively high (Short, et al., 2000).

Applied Microsystems Ltd. (AML) obtained a license for the mass spectrometer developed by the researchers at the University of South Florida. AML is developing the

mass spectrometer for the purpose of commercialization and distribution. For marketing and distribution purposes, they have called the underwater mass spectrometer the "In-Spectr".

Mass spectrometry provides versatility and analytical power due to the wide variety of possible analyses and can arguably be considered the most versatile of chemical sensors. For example, a mass spectrometer has a large dynamic range and can provide the capability to do both ultra-tracing and major constituent detection (Short et al., 2001a). That is, it can detect both large and small concentrations. Major constituents have relatively high concentrations and are often reported as percent concentrations. Ultra-trace constituents, however, are usually on the parts per billion or trillion scale (Short and Kibelka, 2000-2002). Therefore, underwater mass spectrometry is a good choice as a means of chemical analysis in situ. The main challenge, then, becomes how to house the mass spectrometer due to the fact that mass spectrometry must be performed in a vacuum. Further discussion about the uses of mass spectrometers will be presented in Chapter 3.

The Ocean Environmental Risk Engineering using Autonomous Underwater Vehicles (OERE/AUV) research team has recognized the potential for an instrument such as the In-Spectra for use in offshore environmental monitoring, particularly in produced water monitoring. The benefits and limitations of such an instrument need to be understood in order to determine the applicability to offshore operations. This includes determining how well the In-Spectra works in conjunction with AUV technology and whether or not it

can detect the required constituents for produced water monitoring. This piece of equipment was chosen for further assessment.

1.3 LITERATURE/DATA REVIEW

1.3.1 CURRENT SAMPLING METHODS

The Bedford Institute of Oceanography, a division of the Government of Canada, organized a research cruise in June 2000. During the first leg of the cruise, that took place from June 11 to 25, 2000, research was performed at various locations near the Sable Offshore Project and Hibernia. The cruise took place aboard the Canadian Coast Guard Ship, *Hudson*.

The author's participation included the observation of conventional and traditional means of ocean sampling, as well as the performance of the duties for the scientific crew. Information was gained about different existing sampling systems as well as the type of data to be collected for a variety of applications.

Oceanographic data around offshore structures were collected using a variety of samplers and sensors. These instruments were lowered into the water using a winch system on board the ship. Although a variety of samplers were used depending on the samples being collected, all the samplers had the same basic properties. Each consisted of a series of sample bottles that were held open until they reached a certain depth. These bottles were then closed using computer controls on board the ship, resulting in the collection of

a sample. These samples were then returned to the ship and stored for laboratory analysis. In some cases, the on-board laboratory could analyze the sample. For example, the sediment samples collected could be filtered, dried and weighed on board. The main differences in the samplers were centered around the size and orientation of the bottles. Environmental sensors alleviate some of the challenges associated with samplers as they collect information continually while they are in the water. However, these sensors are often deployed vertically from a ship as well. This results in a vertical profile at a single location. When the sensors are not deployed vertically, they are usually towed along a horizontal transect (Saiki and Yano, 2001).

This type of sampling is standard for oceanographic testing. Traditional methods of ocean observations include shipboard profiling and sample collection, as well as cabled instruments and sensor arrays (Griffiths et al., 2001). Rossby (2001) and Saiki and Yano (2001) describe similar sensor and sampling strategies. Each of these papers describes common oceanographic parameters to be studied, including salinity, temperature and current.

Unfortunately, the present sampling strategy using transects leaves gaps in the data. The methods are often viewed as inadequate to meet future continuous real-time monitoring needs (Griffiths et al., 2001). For example, at Hibernia, during the Hudson cruise, the sampling stations were located at distances of 20, 10, 2, 1, and 0.5 kilometres away from the platform on the North, South, East, West and North West sides, yet no samples were

taken in between these locations. Additional information concerning the Hudson Cruise can be found in Appendix A.

1.3.2 Future Sampling Strategies - AUVs

The increasing recognition of ocean variability on all scales necessitates long-term continuous monitoring and observations. Continuous and long-term observations, however, are not achievable by research vessel alone, which in turn, implies the need for automated observation systems (Reeve et al., 2001). Advances in technology, including speed and miniaturization, are modernizing data collection and these trends are expected to continue (Reeve et al., 2001). Griffiths et al. (2001) have described several emerging technologies for oceanographic missions. These technologies include profiling floats, gliders, moored instruments, autonomous surface vehicles, and autonomous underwater vehicles. Millick (2001) states that advances in submergence technology and instruments have revolutionized the ability of researchers to measure chemical, biological and physical processes in the ocean.

AUVs are not a new technology, but most work thus far has concentrated on the vehicle itself, rather than uses such as site investigation (Bingham et al., 2002). However, several authors including Wernli (2000), Westwood (2001), Bingham et al. (2002), and Church and Warren (2002) are now describing the potential uses for AUV technology, including uses in the offshore oil industry.

Wernli (2000) states that offshore oil applications are driving the perfection of Remotely Operated Vehicles (ROVs). As the industry forces the search for oil deeper into the ocean, the need for underwater vehicles increases. Tasks would include support in deepwater pipelines, production, and exploration. The focus will be mainly on depths of about 3000 m immediately, and deeper when the need arises. Wernli also suggests that as the reliability of the autonomy in AUVS increases, the cost will decrease and technology will move in that direction (Wernli, 2000).

Westwood (2001) describes offshore AUV technology as being in a stage of first commercial acceptance, although concerns surrounding commercial viability exist. Applications for uses in the offshore industry are described. The oil and gas industry is rapidly advancing into deeper waters and, as a result, AUVs for deep water surveys are required. Due to the fact that highly manipulative tasks and real time through-water communications are not required on survey missions, survey applications are likely to become the first routine commercial application. Physical demonstration of this was achieved in 1997, and again in 2001 using an early 'Hugin' AUV in the US Gulf of Mexico.

There are considered to be two applications for AUVs with respect to pipelines. The first is pipe lay touchdown where AUVs, and ROVs could be used to monitor pipe laying and relay information to the lay vessel (Westwood, 2001). The other application is a pipeline survey, which is presently the primary application for ROVs. Visual inspections of the

condition of the pipes could be investigated including, debris, depth of burial, and corrosion (Westwood, 2001).

Westwood (2001) also describes geochemical applications where AUVs could be outfitted with sensors to detect hydrocarbons in situ. These AUVs could then be used for exploration. Such uses have not been tested and may not be viable (Westwood, 2001). This type of application, however, might be a viable use for underwater mass spectrometry if the mass spectrometer was designed to be sensitive to hydrocarbons.

Church and Warren (2002) concentrate on using AUVs for archaeological investigation including the use of an AUV as part of deep-water surveys, or in the investigation of shipwrecks.

Bingham et al. (2002) suggests, as well, that AUVS may be able to solve the problems of accurately surveying deep water sites. AUVs could be used to replace more conventional ship-borne hydrographic survey tasks, and to replace conventional ROV tasks. The two major limitations of AUVS were considered to be battery power, and navigation and control. Bingham et al. (2002) have performed missions using two AUVs: the Hugin 3000 AUV developed in Norway, and the Maridian 600 AUV developed in Denmark. Each of the systems carried swathe bathymetry, sidescan sonar, and chirp profilers as payload sensors. The Hugin AUV was used in a deep water mission (2300 m) in the Gulf of Mexico and the Maridian AUV was used in a shallow water mission (80-120 m) in the

central North Sea. Future uses for AUVS in the offshore industry were described to include environmental and engineering inspection (Bingham et al., 2002).

1.3.3 Offshore Environmental Inspection – Potential use of AUVs

When determining the use of AUVs for offshore environmental monitoring typical required parameters for measurement should be considered. The environmental effects monitoring program for the Terra Nova project was considered as an example.

The Terra Nova oil field is located approximately 350 km east-southeast of St. John's, Newfoundland and about 35 km southeast of the Hibernia platform. The project uses a Floating Production Storage and Offloading (FPSO) facility to produce oil at the site. The Terra Nova Development has made a commitment to environmental protection and has therefore developed a detailed Environmental Effects Monitoring Program (EEM) (Terra Nova, 2000).

The Terra Nova Environmental Effects Monitoring (EEM) program provided information about the type of data required for monitoring the effects of produced water offshore as well as traditional monitoring methods. The information provided a basis for comparing existing technology against developing AUV technology. It is an example of the environmental monitoring needs of one particular site. The Terra Nova team plans to monitor sediment and water quality as well as commercial fish species. For this work, only the water quality portion of the EEM plan was considered (Terra Nova, 2000).

As described, continuous and long-term observations are not achievable by research vessel alone. Lee et al. (2000) summarized the toxicity of produced water and indicated that chronic effects may be more important than acute effects, although these potential effects have not yet been studied. He also indicated that there was the potential for the volatile component of chemicals within the produced water to volatize before lab testing could commence, possibly resulting in lower test results. Such indications suggest in-situ sampling strategies using AUVs might be valuable.

Anderson et al. (2000) suggested that other issues, such as nutrient discharges in produced water, have not been studied in any detail. These types of conclusions reinforced both the inference that real data were lacking in the study of produced water discharges and the necessity to evaluate new forms of environmental monitoring for this type of plume detection.

Ramos et al. (2001) have considered the use of AUVs for plume detection. Previous field studies of sewage outfall plumes indicate a complex and patchy structure, although, it is unknown whether this is due to physical processes or measurement limitations (Ramos et al., 2001). One strategy used for sewage plume monitoring is sampling at discrete locations, which does not adequately define the spatial extents of the plume (Jones et al., 2001).

To try to gain better spatial information, towed payloads carrying a package of sensors have become typical sampling strategies. Such strategies are described by Jones et al.

(2001), CDM (2000), and EPA (2001). Each of these papers describes a towed package for a sewage outfall plume study that contained standard oceanographic equipment such as a CTD (conductivity, temperature, depth) sensor, a transmissometer, used for determining light transmission, which in turn provides information regarding the amount of suspended material in the plume, and a fluorometer, which detects fluorescent material in the water column. The fluorometer was used to detect the plume tracer Rhodamine Dye that was used in each study.

Towed studies are still, however, not used without limitations. It has been suggested by Ramos et al. (2001) and Jones et al. (2001) that AUV technology could likely be an efficient means of collecting outfall sewage data if an effective sampling strategy was in place.

Mass spectrometry is a powerful analytical technique that has been used for almost a hundred years. It is a common chemical analytical technique, although it is usually a laboratory procedure. Harsh environment mass spectrometry, including underwater mass spectrometry, is increasing in popularity and progress is being made in the miniaturization of such instruments (Short et al., 2000-2002). An innovative underwater mass spectrometer was presented by Short et al. (2000). This instrument has the capability of measuring chemical parameters in-situ to 200 atomic mass units (amu). Applied Microsystems Ltd., in Sidney, British Columbia, has purchased an exclusive licensing agreement to commercialize and distribute the mass spectrometer, with the name In-Spectr. Although it was this instrument that was chosen for further

investigation, it is not the only underwater mass spectrometer that has been designed. Camilli and Hemond (2001) presented another underwater mass spectrometer designed at the Massachusetts Institute of Technology. This system can analyze dissolved gases to 100 amu (Camilli and Hemond, 2001).

CHAPTER 2 TRACER STUDY

2.1 BACKGROUND: CHOOSING THE TEST LOCATION

The first step in the preparation of the testing phase for the sea-trials was to determine the location. It was decided that the Burrard Inlet in Vancouver, BC would be the most convenient location for testing. The main reasons for this decision were that this location is close to the ISE docks where the ARCS vehicle is stored, it is easily accessible, and the research vessel used to deploy the ARCS vehicle is located there. The logistics of moving the ARCS AUV elsewhere were not feasible.

An objective of this project was to test a payload, on an AUV, that could be used for environmental discharge monitoring. In order to demonstrate the uses of the mass

spectrometer on the AUV, a plume containing a chemical tracer needed to be present in the water column at the test location. Another reason for choosing the test location was that the Burrard Thermal Generating Station (BTGS) is located nearby, which discharges a cooling water effluent, producing a plume, which was considered a test possibility.

The generating station shut down its operations temporarily in the late fall of 2001 and was not in operation during the sea trials. Although the BTGS was not operational during the final test, it played an important role in determining the concentration of tracer required for the experiment. For this reason, the BTGS is included in the discussion.

2.2 EFFLUENT COMPOSITION CONSIDERATIONS

When considering plume delineation studies and the use of tracers, the effluent characteristics must be considered first. Effluents are physically and chemically different than their receiving environment, and can often be traced once they are discharged. The BTGS cooling water plume was investigated to determine whether there were any chemicals present that could potentially be used as tracers. The permit issued by the British Columbia Ministry of Environment and Lands for the BTGS cooling water discharge discusses briefly the acceptable characteristics of the cooling water plume. In this permit there are two chemical categories listed for the plume. The first is the concentration of chlorine in the cooling water, which must be less than 0.02 mg/L, and the second is the concentration of 'oil and grease', which must be less than 10 mg/L. 'Oil and grease' were deemed inappropriate tracers, as they are very loosely defined as being anything extractable by hexane (Phillip Analytical Services, 2002). Such chemicals can

contain anything from animal fat to diesel oil and are therefore difficult to target for detection. It was also determined that the chlorine discharge concentration was not high enough to be detected. The BTGS is almost always discharging its chlorine at levels lower than 0.01 mg/L (10 ppb), which is the detection limit used by the plant (Brotherston, 2001). Although the mass spectrometer has a detection of about 5 ppb it was assumed that any additional dilution, with distance from the outflow, would bring levels well below this limit. Therefore, it was decided that an added tracer should be considered.

2.3 TRACER QUALITIES

An ideal contaminant to use as a plume tracer has near zero background levels and is a conservative substance. This means that it has a low decay rate and can therefore be measured in very low concentrations in the field. The preferred type of tracer for field studies according to Environment Canada is a fluorescent dye. The recommended dye is Rhodamine WT. This dye has been proven to be a non-mutagen, to have low potential for toxicity and for adverse effects in the aquatic environment, and to be readily measured in the field in the low grams per litre range of concentrations. In addition, it is a safe chemical when handled with care, and almost always has near-zero background levels (Environment Canada, 2001).

For this project, however, there was an additional consideration when choosing a tracer: it had to be compatible with the mass spectrometer. The types of chemicals that can be measured by the mass spectrometer will be discussed in the mass spectrometer section of

this thesis in Chapter 3. Two of the main limitations were that the chemical of choice could not be more than 200 atomic mass units, and that it had to be relatively non-polar, that is the solubility in water needed to be relatively low (AML, 2000-2002).

2.4 TRACER DETERMINATION

2.4.1 SUMMARY OF CONSIDERED TRACERS

Rhodamine Dye WT was eliminated as a tracer choice as it does not meet the constraints set by the mass spectrometer. It fails to meet the atomic mass constraint, as its atomic weight is 567 (IPCS, 1998).

Further research was performed to determine whether there was another possible chemical that could be used for tracing the plume. Approval for a permit to add a tracer to the discharge would be more likely given where a Canadian environmental authority had already approved the tracer of choice. Environment Canada has a document outlining the procedures for studying pulp and paper effluents. Environment Canada (2001) states that where the use of Rhodamine dye was not possible, other chemical tracers may be considered. The document is missing crucial information about these other possibilities. Environment Canada (2001), mentioned sulphur hexaflouride (SF_6) as one possible non-rhodamine tracer, although no further information was present.

2.4.1.1 Non-Rhodamine Tracers

Information about tracer studies using tracers other than Rhodamine dye is very limited. The information in this section is included to show the procedure used to determine the tracer of choice, and to summarize and demonstrate what little information exists on non-rhodamine tracers. A pollution control assessment scientist with the Industrial Programs of Environment Canada was contacted to gain additional information on the missing information from Environment Canada (Boyd, 2001). Environment Canada was unable to add information on the missing chemical tracers, but did provide further contacts that have expertise in the field.

Dr. Terrence Donoghue, an engineer with the Woods Hole Oceanographic Institute in Massachusetts, USA has done chemical tracing work using sulphur hexafluoride. A personal communication with Dr. Donoghue revealed information about the use of sulphur hexafluoride as a tracer. Sulphur hexafluoride is most often used as a tracer during long-term testing. Usually, this means testing done in the time frame of a year rather than short-term tests in the range of hours, such as those performed for this project. Sulphur hexafluoride, a gas, must be compressed to pressures in the order of 10^6 kPa in order to be introduced to a water stream. This was not a feasible option for this project (Donoghue, 2001).

Short and Kibelka (2000-2002) have previously performed successful tests with their version of the mass spectrometer using dimethyl sulphide. After eliminating Rhodamine

dye and determining that there were no other feasible options, it was decided to use dimethyl sulphide as the tracer of choice.

2.4.1.2 Dimethyl Sulphide

Dimethyl Sulphide (DMS) meets the chemical criteria for the mass spectrometer. Dimethyl Sulphide is an important sulphur-containing atmospheric trace gas of marine biogenic origin. It is produced by some classes of marine phytoplankton (Gabric *et al.* 1993). Toxicological information provided by Material Safety Data Sheets indicates that DMS is not considered to be a hazardous substance in Canada or the United States (Fisher Scientific, 2001). The next step was to determine the quantity of tracer that had to be added.

2.4.2 TRACER QUANTITY

2.4.2.1 Objective

The aim of adding a tracer was to introduce to the plume something that the mass spectrometer could detect at some distance from the source. Short and Kibelka (2000-2002) had success detecting DMS at levels of about 1 ppb to 5 ppb. A challenge for this thesis work was determining the quantity of tracer to be added to the water in order to detect the plume and the best method of introducing the tracer to Burrard Inlet. It was assumed that the BTGS outfall would be the most appropriate method of introducing a tracer.

The properties of the BTGS plume needed to be considered in order to effectively determine the required tracer volume. Although the BTGS was not operational during the testing, it was the basis for determining the tracer volume. The total tracer volume remained the same, although a different method of introducing it to the inlet was chosen.

2.4.2.2 Effluent Considerations

The BTGS has four outfall pipes, two in an easterly direction and two in a westerly direction. The maximum total discharge for the BTGS is 1.7 million m^3 of water per day. This maximum flow was used for all calculations and assumptions, so that maximum dilution of the tracer was considered. It was also assumed that the tracer would only be added to a single pipe. Each pipe is 2.5 m in diameter (Brotherston, 2001).

2.4.2.3 Previous Study

A consulting firm in British Columbia, Seaconsult Ltd., performed a study using Rhodamine dye in the BTGS effluent in 1990. They chose to use 27 L over a three-hour period for that study (Brotherston, 2001). Using that value, the concentration of DMS that would be present in the effluent flow was calculated. It was assumed that the maximum flow rate would be divided evenly over 4 pipes. These calculations are shown here:

Equation 2-1: Single Pipe Flow

$$1.7\text{x}10^{6}\ \frac{\text{m}^3}{\text{d}}\ \text{x}\ \frac{1}{4\text{pipes}}\ \text{x}\ \frac{1\text{d}}{24\text{h}}\ \text{x}\ \frac{1\text{h}}{3600\text{s}} \cong 5\text{m}^3/\text{s}$$

Equation 2-2: Total Volumetric Flow of DMS per Hour

$$\frac{27\text{L}}{3\text{h}} \text{x} \frac{1\text{m}^3}{1000\text{L}} \text{x} \frac{1\text{h}}{3600\text{s}} = 2.5\text{x}10^{-6}\,\text{m}^3/\text{s}$$

Equation 2-3: Total Concentration of DMS per Hour:

$$\text{Concentration} = \frac{2.5\text{x}10^{-6}\,\text{m}^3/\text{s}}{5\text{m}^3/\text{s}} \text{x}10^9 = 500\text{ppb}$$

The dilution of the effluent in the inlet immediately after discharge had to be considered in order to determine the concentration at that time. The purpose was to determine whether the concentration after initial dilution was high enough for the mass spectrometer to detect. A minimum concentration value of 5 ppb was considered acceptable.

The initial dilution of a plume is considered to be the dilution that takes place between the moment of discharge until the plume reaches its maximum height. For an unstratified water column, this is the dilution that occurs between discharge and the time it takes the plume to reach the water surface (Mukhtasor, 2001). To determine the initial dilution, the Cornell Mixing Zone Expert System (CORMIX) model was used. This model was developed between 1985 and 1995 under a co-operative funding agreement between the US EPA and Cornell University. The model is divided into three sub-models. CORMIX 3 for buoyant discharges was chosen for this example as it best suited the problem in question. The inputs and outputs for this model are shown in Appendix B. The initial dilution was found to be 2.4%. This resulted in a DMS diluted concentration of 12 ppb, which was considered acceptable, as it was higher than the 5 ppb limit set above.

A request was submitted to the BC Ministry of Water, Land and Air Protection for a permit to add DMS to Burrard Inlet at a maximum rate of 27 L during a 3-hour period. This volume was based on the assumption that the tracer would be added using the plume from the BTGS. It was stated in the permit that the tracer would be added to the BTGS plume, or directly to the inlet from the ship should the BTGS plume be unavailable. The permit was approved and, as the BTGS shut down its operation, the tracer was added directly to the inlet from the ship.

CHAPTER 3 EXPERIMENTATION

3.1 PRELIMINARY PREPARATIONS

3.1.1 DETERMINING THE TEST LOCATION

The previous chapter outlines the reasons that Burrard Inlet was chosen for the test location. The location was close to the ISE docks where the ARCS vehicle and research vessel were stored, and it was easily accessible. The logistics of moving the ARCS AUV elsewhere were not feasible.

3.1.2 MEASUREMENT CRITERIA

3.1.2.1 Temperature

The next step in preparing the test setup was to determine what parameters would be used to delineate the plume. In the case of the BTGS, there is a known temperature difference between the intake water and the cooling water outfall. The temperature difference is a result of the heat transfer that occurs during the cooling process used in the plant. For this reason, it was decided that a conductivity, temperature and depth sensor (CTD) would be added to the payload to detect the temperature differences.

Although the generating station was not operational during the sea trials, the CTD was left on board the AUV. The data were used to complement those collected by the mass spectrometer. The natural salinity and temperature changes were observed.

3.1.2.2 Chemical

In order to demonstrate the uses of a mass spectrometer, a chemical should be present for the mass spectrometer to detect. The chemical of choice was dimethyl sulphide as it met all the constraints for a chemical tracer, as discussed in Chapter 2. In brief, these were that the chemical be non-toxic to the marine environment, be less than 200 atomic mass units, and have low background levels. It was determined that the dimethyl sulphide (DMS) would be added at a maximum concentration of 9 L/h (2.5×10^{-6} m^3/s), which was set by the BC Ministry of Water, Land and Air Protection. The chemical was purchased and ordered from Sigma-Aldrich Canada (product number 27,438-0). The process by which this chemical was chosen was discussed in Chapter 2.

A permit to use DMS in Burrard inlet was obtained from the BC Ministry of Water, Land and Air Protection. The Vancouver Port Authority was also informed of the sea trial plans and their permission was obtained.

3.1.3 ARCS Preliminary Preparation

Preparation of the ARCS vehicle was done primarily by ISE with input provided by the author. This input consisted mostly of the details concerning the requirements of the analytical equipment.

In preparing ARCS, an additional length of 1 foot was added to the payload bay of the vehicle. This was necessary, due to the fact that the original payload bay was not long enough to hold the mass spectrometer. This was started on October 24, 2001. At this time, weight and balance sheets were revised, and new lead weights were cast and installed in the ARCS nose section. Figure 3-1 shows the location of the payload bay and the nose cone of the ARCS vehicle. The white section of the payload bay is the length that was added.

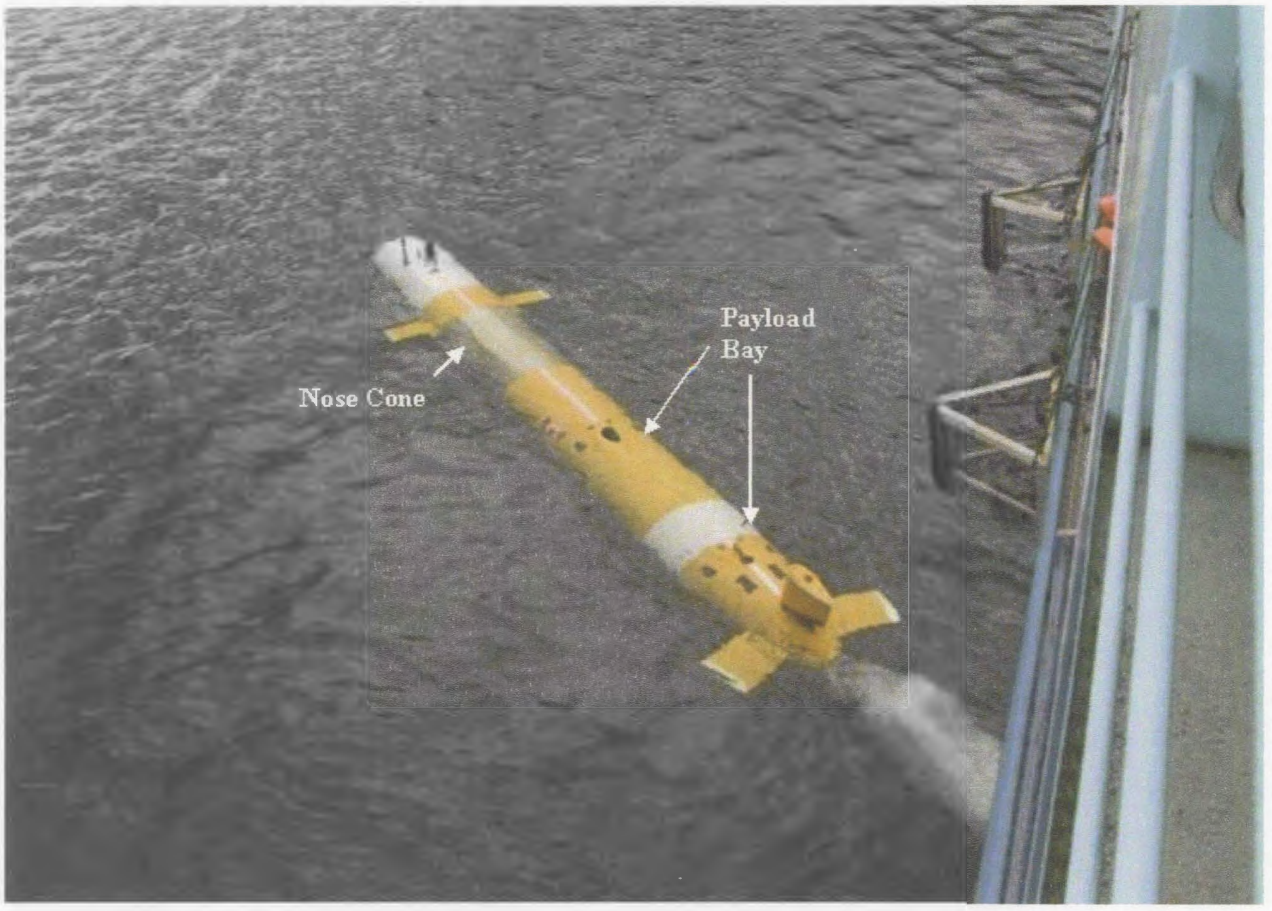

Figure 3-1: Location of Payload Bay and Nose Cone on ARCS Vehicle

On January 21, 2002, ARCS was moved to the Researcher vessel at Berry Point wharf. The first pre-dive was completed on January 22, 2002. The weight and balance was evaluated. The emergency fault system was tested and determined to be functioning properly. The attitude and thruster controls were also checked and the power consumption was evaluated.

Other predives were performed with ARCS during the week of January 21, 2002 by the ISE support staff. The tail section was light, so buoyancy (24 lbs) was removed from this

section by removing floats that had previously been installed in the ARCS vehicle to add extra buoyancy. Due to battery age, speed was limited during the sea trials, which caused the planes to be less effective. This resulted in a greater sensitivity to weight and distributions (ISE, 2000-2002). All basic piloting functions were tested and determined to be acceptable. ARCS was put into mission mode for two hours. The mission was executed properly after a few minor adjustments.

After the predives, the analytical equipment was installed. The mass spectrometer was held in place by two identical mounting blocks. These blocks were designed to fit the radii of both the ARCS vehicle and the mass spectrometer. They were composed of two pieces. The outer diameter of the block sat in the payload bay and was securely bolted using five 3/8" cap screws. Four additional screws held the second and top piece of the block firmly to the first. A small layer of neoprene foam lined the inside of the block, which ensured a snug fit around the mass spectrometer and prevented damage to the casing of the equipment. Figure 3-2 shows the mounting block design. Figure 3-6 shows a picture of the mass spectrometer mounted in the payload bay of ARCS.

The CTD Micro Sensor was mounted vertically in the nose cone of ARCS. As part of the preliminary ARCS preparation, a slot was cut in the nose cone that allowed the nose cone to slide directly over the CTD. Applied Microsystems Ltd supplied mounting blocks for the CTD.

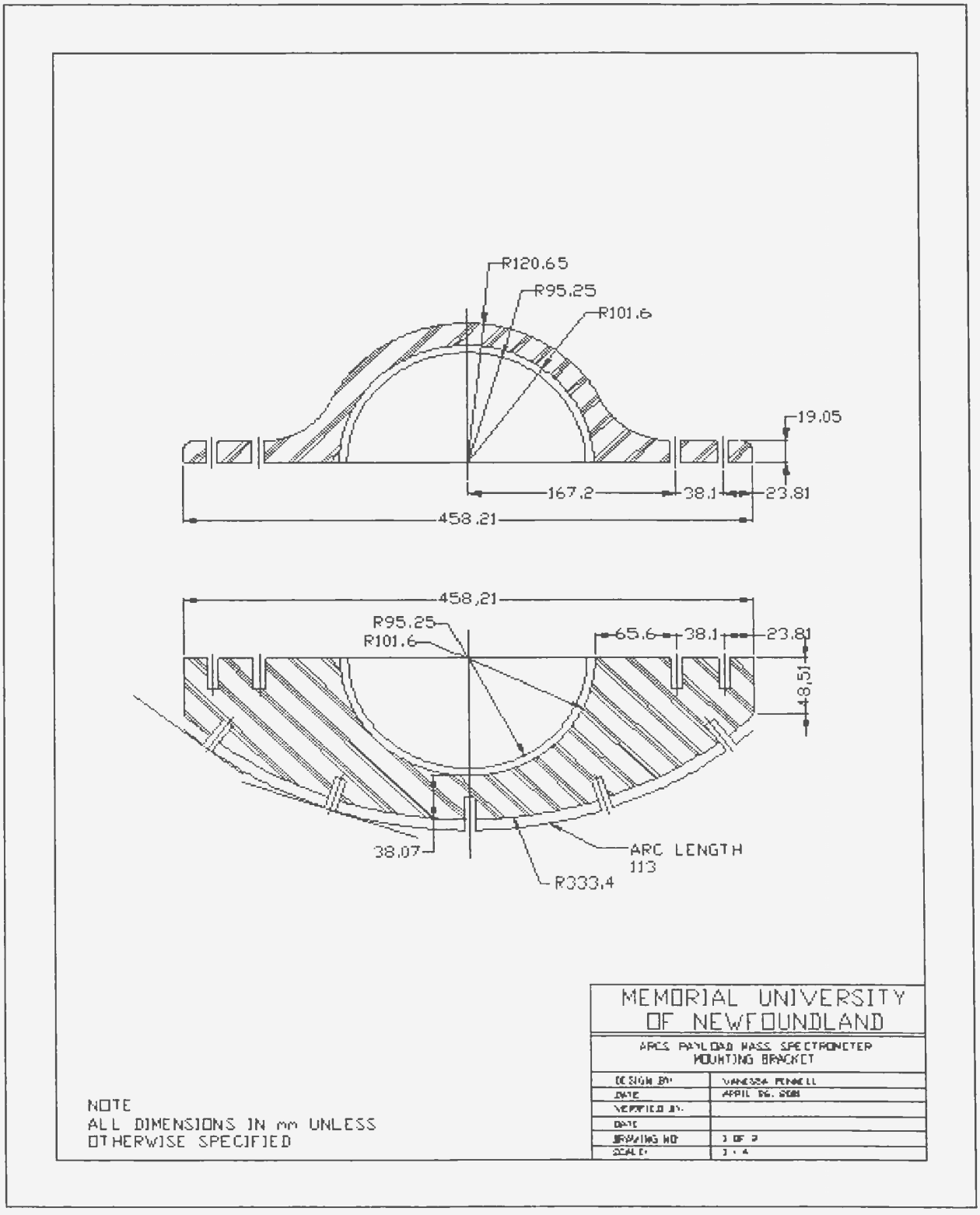

Figure 3-2: Mounting Blocks for In-Spectr in ARCS Vehicle

3.2 MASS SPECTROMETRS AS IN-SITU SAMPLERS

Mass spectrometry provides versatility and analytical capability due to the wide variety of possible analyses. For example, a mass spectrometer can provide the capability to do both ultra-tracing and major constituent detection. Essentially, this means it has a wide range, detecting chemicals in very low concentrations to very high concentrations. Therefore, underwater mass spectrometry is a good choice as a means of chemical analysis *in situ.* It is arguably the most versatile of chemical sensors (Short et al., 2001b).

Mass spectrometers are capable of extremely high sensitivity, isotopic resolution and wide dynamic range. Mass spectrometers can measure the relative abundance of different isotopes of elements (atoms that have the same number of protons in the nucleus, but different numbers of neutrons) and therefore can measure the relative abundance of these isotopes in molecular species as well. An example is carbon dioxide (CO_2). The most abundant isotope of carbon is 12C (6 protons, 6 neutrons), but 13C (6 protons, 7 neutrons) is present at around 1%. A mass spectrometer is capable of separating and measuring both isotopes (Short and Kibelka, 2000-2002).

Field-portable units have the capability to revolutionize ocean sciences (McMurtry and Smith, 2001). The In-Spectr is an example of one such portable unit. The problems with designing such a system, especially one that is low power and useful for long periods of time underwater, are centred around three basic problems: sample introduction, vacuum maintenance and power consumption (McMurtry and Smith, 2001).

3.2.1 IN-SPECTR

The underwater mass spectrometer that was used for this project has the product name "In-Spectr". It was supplied by Applied Microsystems Ltd. (AML), a Canadian company that specializes in underwater instrumentation. The In-Spectr was developed at the Center for Ocean Technology at the University of South Florida, which is an engineering organization aimed at developing innovative marine sensors and instrumentation. Due to a lack of adequate equipment in the commercial marketplace, the Center for Ocean Technology undertook the task of developing an in-situ mass spectrometer as a future payload for AUVs. They chose the mass spectrometer as the sensor of choice due to the breadth, versatility and power of the technology. AML secured a licensing agreement with the University of South Florida for the commercialisation and distribution of the instrument. The mass spectrometer tested in this thesis was the first production version of this instrument.

3.2.1.1 Meeting the Needs of Underwater Mass Spectrometry

As described above there are three major challenges when designing miniaturized, autonomous underwater mass spectrometers. The first of these is sample introduction. This problem was overcome in the In-Spectr by using a membrane induction system (Short et al., 2001b). This system is based on a silicone membrane introduction interface coupled to a quadrupole mass filter for detection and quantification of volatile organic compounds (VOCs) and dissolved gases to 200 atomic mass units (amu) at parts-per-billion (ppb) levels. A quadrupole mass filter uses only electric fields to separate ions through their mass to charge ratio (m/z). A quadrupole consists of four metal parallel rods

or poles through which the ions being separated are passed. The poles have a fixed Direct Current (DC) and alternating Radio Frequency (RF) voltages applied to them. Depending on the produced electric field, only ions of a particular m/z will be focused on the detector, all the other ions will be deflected into the rods. By varying the strengths and frequencies of electric fields, different ions will be detected thus making the mass spectrum (Cambridge University Chemical Laboratory, 2000). Figure 3-3 shows the basic configuration of a quadrupole mass filter. Membrane introduction is an efficient means of transporting volatile non-polar species from the water column into the vacuum system of the mass spectrometer.

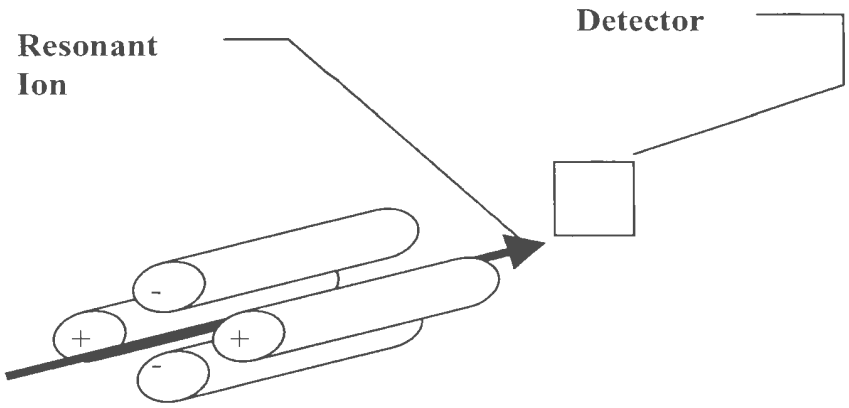

Figure 3-3: Quadrupole Mass Filter

The next challenge to underwater mass spectrometry, and perhaps the most difficult to overcome, is vacuum system management. Most vacuum pumps ultimately compress pumped gases and exhaust them at atmospheric pressure. This is problematic inside a closed pressure vessel system. If the pressure at the vacuum pump exhaust port increases substantially above atmospheric pressure, the performance of the pump will degrade. This problem has been alleviated in the In-Spectr by isolating the final stage of pumping

inside a separate pressure vessel. This vessel is pre-evacuated to approximately one-quarter of one atmospheric pressure prior to deployment for continuous underwater operation in excess of one week. The high vacuum required for the mass spectrometer is created in a two-stage process. In the first stage, roughing pumps were used to create a vacuum with pressures near 1 to 10 Torr (133 – 1033 Pa) range. A turbo molecular pump was then used to achieve high vacuum at pressures near 10E-6 Torr (0.00133 Pa).

The In-Spectr meets the third challenge, which is to minimize power consumption. The entire system is powered by 24 VDC and consumes less than 95 Watts with all components in operation.

3.2.1.2 Physical Design

The underwater mass spectrometry system used for this mission is a single instrument consisting of three segregated pressure vessels. The front vessel serves as the sample collection system and contains a pump and a flow injection system. There are two modes of operation. In one mode, sample water is continuously pumped into a 1-mL sample loop, the contents of which are periodically swept into the membrane introduction mass spectrometer (MIMS) system in the central vessel by switching the flow injection valve. Pumping deionized (DI) water from a reservoir bag into the MIMS interface probe displaces samples. In this manner changes in ion intensities for selected masses can be continually compared to baseline levels in the mass spectrometer. Figure 3-4 shows a flow diagram for this continuous flow mode.

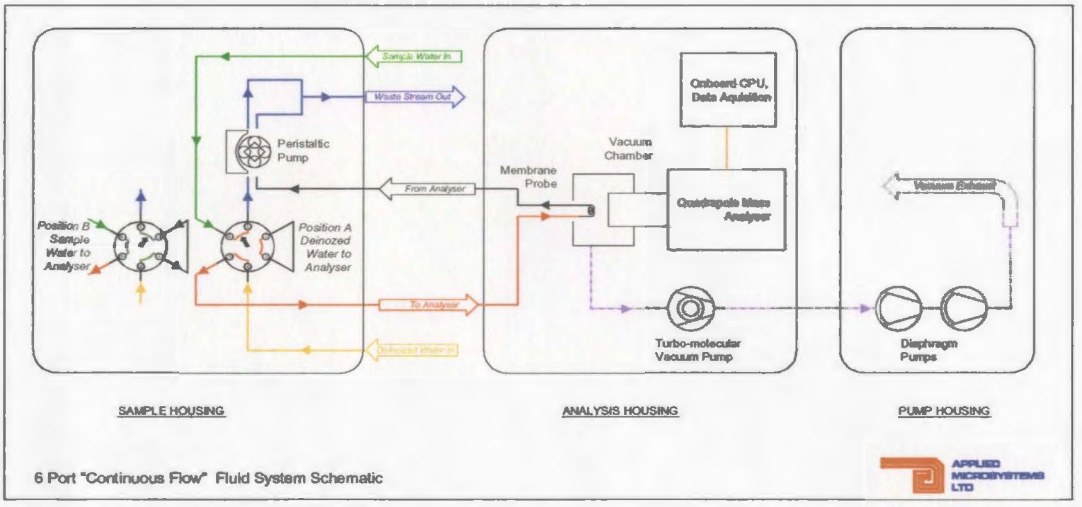

Figure 3-4: "Continuous Flow" Flow Diagram for the In-Spectr, from AML, 2002

The second mode, and the method of choice for this project, is the continuous mode of sampling. This type of sampling eliminates stream switching, and decreases lag time between sample intake and analysis. The continuous sample mode does not compare samples against a baseline level to give discrete values. Instead, it detects the presence or absence of the contaminant (DMS) in the water column as the mass spectrometer is moved through the water. That is, the mass spectrometer will show a straight horizontal line until DMS becomes present, in which case a peak will form. This is shown in the data in Chapter 4.

The central pressure vessel contains the main components of the mass spectrometer system. These components include the vacuum chamber, mass analyser, membrane introduction probe, associated electronics, turbo molecular vacuum pump, Pentium based

CPU card, 700MB hard drive, and a power distribution board. The power distribution board was interfaced with an external computer prior to deployment, which activated the various components in sequence.

The third vessel contains two dry diaphragm pumps in series that serve as roughing pumps for the turbo pump. This chamber also acts as the reservoir for vacuum pump exhaust gas.

The practical depth of deployment for this system is presently limited to 10 metres. However, current development work is in progress to deploy the system at increased depths of 200m. The weight of the entire system is 378 N in air, yet is just 24.5 N in seawater. The overall dimensions are 138 cm in length and 19 cm in diameter (AML, 2000-2002).

3.2.1.3 In-Spectr Preliminary Setup

There were two modes of preparation for the mass spectrometer. The first was the initial system testing and verification that the individual components were operating properly, followed by the complete system integration. Secondly, the mass spectrometer was prepared for the deployment. The staff of Applied Microsystems Ltd completed these preparations before the sea trials.

1) The first part of mode one was to test the pressure housings. The housings for both the pump and the sample and analysis were tested in 13 m of water. This depth was adequate to prepare for the planned deployment depth. Secondly, the

membrane was cycled multiple times to 10 m water pressure, approximately 200 kPa using nitrogen gas. Next, the analyzer was used with standard samples, with known results. This ensured that the analyzer was working properly. The fourth step was to test the switching valve that is used to switch between the deionized water stream and the sample flow stream when testing against deionized water. The vacuum purging system and high vacuum integrity were then checked. Finally, the sixth step was to check continuous pump operation for up to a 48-hour period.

2) In the second mode of testing, the mass spectrometer was prepared for this specific deployment. First, the plumbing system was adjusted for direct sampling as during this test the mass spectrometer was used in continuous mode. Next, a 5-micron inlet filter and mount was designed and installed for attaching the inlet tubes to the hull of ARCS. This mount was used to keep the inlet tube rigid and filtered. In addition, this ensured that the intake tube was in the same position throughout the trials. Thirdly, a diode system was installed to provide constant power of 24 V to the mass spectrometer. Essentially, this diode ensured that there was no power interruption when switching from shore power to ARCS power. The diode automatically switched from each source depending on which was available. The fourth and final preparation for the mass spectrometer was the design of a waterproof cable casing. At the time of deployment the underwater computer cables were not available. To replace this, a waterproof housing was designed to keep the cables dry.

3.2.1.4 In-Spectr Operation

Preparing the mass spectrometer for deployment was a five-step process controlled through the In-Spectr software on-board the internal mass spectrometer computer. The user interface is through a laptop, which accesses the on-board CPU via an Ethernet link. The software package guides the user through the boot-up process for the mass spectrometer. The boot screen is shown in Figure 3-5.

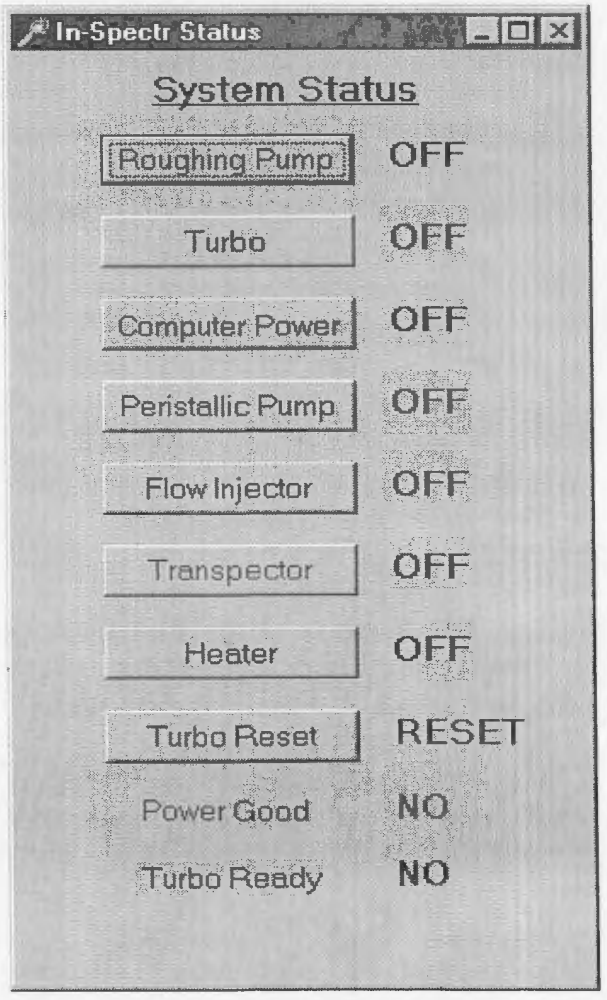

Figure 3-5: In-Spectr Software Start-Up Screen

Each button or tab shown in Figure 3-5 was pressed to start the indicated procedure. The status indicator on the right turns green when the associated system is ready. The complete system start-up is described in the steps below.

1) System start-up requires operating only the roughing pumps to evacuate the ionization chamber to pressures in the range of 1 to 10 Torr. This is because turbo molecular pumps typically require inlet pressures that are in the millitorr range to achieve maximum speed and performance. The ionization chamber was then pumped (or evacuated) into the exhaust chamber creating a slightly positive pressure in the exhaust chamber. The flow was then changed using a switching valve built into the In-Spectr's outer end cap. This step simultaneously pumped the exhaust chamber gases to atmosphere, creating a vacuum in the exhaust chamber, which acts as a reservoir for sampled gases. The valve was then switched back, sealing the vessel and flow stream from outside, and re-routing the exhaust gas stream back into the exhaust chamber. This evacuation process was required once for the three days of sea trials.

2) The turbo pump was started to force the system down to pressures required for the gas analyser to operate. Most quadrupole based gas analysers require a vacuum in the 10E-6 torr range. During turbo pump start-up, the pump speed was monitored until it reached its maximum. This is an automatic seven-step process that can take anywhere from two to forty minutes depending on ambient

temperature and previous vacuum levels in the chamber. The indicator light on the system activation software ensures that the turbo pump is ready.

3) The next step involved the start-up of the on-board computer inside of the In-Spectr. This took place after initial start-up of the turbo pump to prevent risk of damage from any power surge. The on-board computer provided communication between the external laptop and gas analysis software, and provided control over the fluid switching valve if used in that mode. The computer also stored the data collected by the mass spectrometer during its mission.

4) The fourth step of the start-up process was to turn on the peristaltic pump. This provided liquid pumping of the sample stream through the membrane interface. A test sample of distilled water is pumped through to ensure liquid flow.

5) A data-logging file was created. Data from the gas analysis software is logged and written to the hard-drive in real time.

3.2.1.5 Calibration of the In-Spectr

The mass spectrometer was calibrated well before test time as previously explained. Standard samples were sent through the analyzer to ensure that it was working properly.

On the day of the test, to ensure that the mass spectrometer was still functioning properly after integration into the ARCS vehicle, a test sample of toluene was analyzed. As the

mass spectrometer was set up for continuous sample mode sampling this test sample was not used to determine a specific concentration, but rather to ensure that the analyzer recognized the change in concentration once the toluene was added. Continuous sample mode sampling by-passes comparison against a baseline level, and shows only that the chemical is present and gives no indication of its concentration.

Only a small sample of toluene was needed, as the detection limits on the mass spectrometer are in the parts per billion range. To get a small sample, a wooden stick was dipped in a concentrated toluene sample and then was used to stir distilled water. This added a small amount of toluene to the distilled water, which was then sampled by the mass spectrometer using the inlet tube. The amount of toluene absorbed by the wood was enough for the mass spectrometer to detect. Real time monitoring was used to view the concentration line on the laptop that was connected to the mass spectrometer. Once the toluene sample reached the analyzer, a peak showed on the computer screen. This confirmed that the analyzer was detecting.

The time for the sample to go through the mass spectrometer into the analyzer was also recorded using a stopwatch. The stopwatch started when the toluene sample was added to the inlet tube, and the time was stopped when the peak began to show on the computer screen. This was done several times and a consistent time of sixty seconds was recorded. Therefore, sixty seconds was taken to be the time lag between sample location and analysis time.

3.3 CTD INSTRUMENTS AS IN-SITU SENSORS

CTDs are used as in-situ instruments for a variety of reasons. Most commonly they are used to detect hydrothermal plumes and vents (NOAA, 1998). They are used to measure physical characteristics in the water column, which may be an indicator of water quality, and changes in the ocean environment (Terra Nova, 2000). They are common instruments in oceanographic studies.

3.3.1 MICRO-CTD SENSOR

The Micro-CTD is a combination of three individual sensors from Applied Microsystems Smart Sensor Series, integrated into a single housing unit. This series was designed to have standard electrical, mechanical, and communications features to easily allow integration into autonomous and remotely operated underwater vehicles. The sensors in the series include temperature, pressure, conductivity, and sound velocity sensors (AML, 2001).

The Micro-CTD was designed to operate from any DC supply between 8 and 20 volts. For the deployment, the sensor was powered from a 3.6 V lithium battery. It is controlled by a software package called "Smart Talk Software", designed by Applied Microsystems (AML, 2001).

An advantage to the system is that the instrument can output data in a raw data format or in engineering units. Another advantage is that the Micro- CTD can output a single scan of data or a continuous stream of data at the maximum scan rate of 25 scans per second. For this mission, the CTD scanned at a rate of one scan per second (AML, 2001).

3.4 TEST SET UP

3.4.1 MOUNTING THE ANALYTICAL EQUIPMENT

The mass spectrometer was brought on board the ship using a sling attached to a crane on the foredeck of the Researcher on January 31, 2002. In order to confirm the buoyancy of the mass spectrometer, the mass spectrometer was attached to a hanging scale and lowered into the water using the crane. It was confirmed that the weight of the mass spectrometer in air was about 88 pounds and less than 5 pounds in water. It was determined that it was not heavy enough to be a concern to the overall buoyancy of the underwater vehicle.

The mass spectrometer was then added to the payload bay of the ARCS vehicle. It was held in place by two identical mounting blocks previously described and shown in Figure 3-5. These blocks were designed to fit the radii of both the ARCS vehicle and the mass spectrometer.

The bottom portion of the blocks was bolted to the ARCS payload bay. The mass spectrometer was then lifted into the payload bay by hand and laid in the blocks. The top portions of the mounting blocks were then placed over the mass spectrometer and securely bolted to the bottoms. Figure 3-6 shows a picture of the mass spectrometer mounted in the payload bay of the ARCS vehicle, although the top portions of the mounting blocks were not yet added.

Figure 3-6: In-Spectr Mounted in ARCS, February 2002

The sample intake tube was placed outside of the ARCS vehicle at the top of the hull in the payload module. Figure 3-7 shows a picture of the intake tube in the hull of ARCS.

Figure 3-7: Sample Intake Tube for Mass Spectrometer

The CTD Micro Sensor was mounted vertically in the nose cone of ARCS. A slot was cut in the ARCS nose cone, which allowed the nose cone to slide directly over the CTD. The CTD was then placed in the vehicle and secured using a clamp designed by Applied Microsystems to fit the CTD. As a safety strap to prevent vertical sliding, a cable tie also attached the CTD to the nose cone. Figure 3-8 shows the CTD mounted in the nose cone.

Figure 3-8: CTD Mounted in Nose Cone of ARCS, February 2002

3.4.2 TRACER DISPENSER SET UP

The next step in the set up was to get the tracer into the water. To do this, a Mazzei® flow injector was used. This is a venturi-type injector. A pressure difference between the inlet and outlet creates a vacuum inside the injector body that initiates suction through the suction port (MIC, 2001). When a pressurized fluid enters the inlet, it is constricted toward the injection chamber, which forces it to change into a high velocity jet stream. This velocity increase results in a pressure decrease, creating suction through the injector port enabling another fluid to be added to the flow. The jet stream is then diffused

toward the injector outlet where its velocity is reduced again and converted into pressure energy, although at a lower pressure than at the inlet (MIC, 2001). A diagram illustrating the Mazzei® injector is found in Figure 3-9.

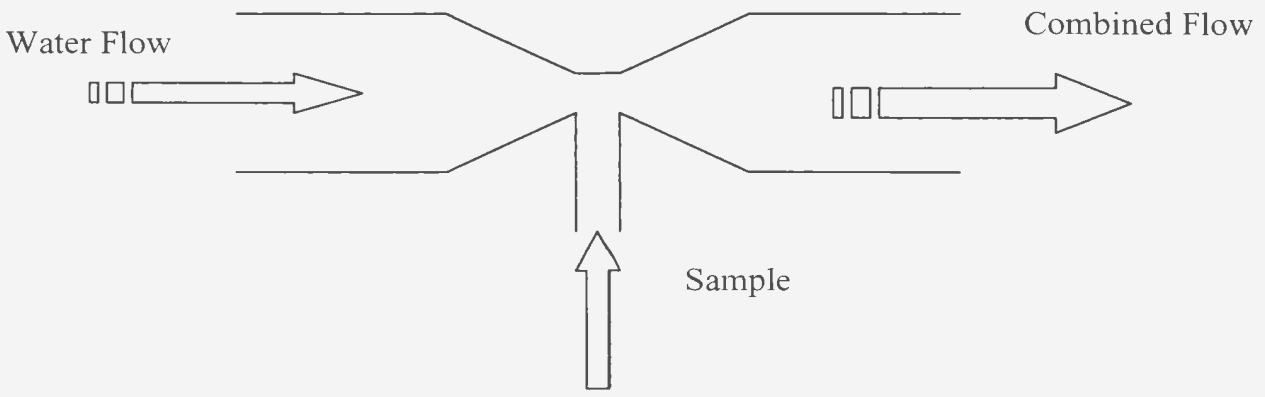

Figure 3-9: Flow Diagram of the Mazzei® Injector, based on MIC (2001).

A submersible pump was used to pump seawater from Burrard Inlet through a hose and into the Mazzei® Injector. The DMS was sucked through the injection chamber, and then the combined flow was pumped through a copper pipe down into the ocean, at a depth of about 10 m. The tracer was injected into the water on each trial day in this manner. To allow time for the DMS to disperse through the inlet, the start time for injection was about 10 minutes before the start of each mission, usually while ARCS was piloting to its first waypoint. The tracer was injected continually until the end of each trial.

A major concern for all components of the tracer introduction system was the fact that DMS is an excellent solvent for a wide variety of inorganic and organic chemicals. Often, it can be used as a solvent for polymers. For this reason, it was important to ensure that

only metal fittings were used for the plumbing to get the DMS into the water. The Mazzei® Injector, however, was the only exception to this rule. It is made of polyvinylidene fluoride KYNAR. This material is compatible with DMS. Figure 3-10 shows the tracer dispenser setup. The black hose is connected to the submersible pump. The smallest copper pipe draws the DMS into the injector (covered by duct tape) and the larger copper tube pumps the combined flow back into the ocean to a depth of about ten meters.

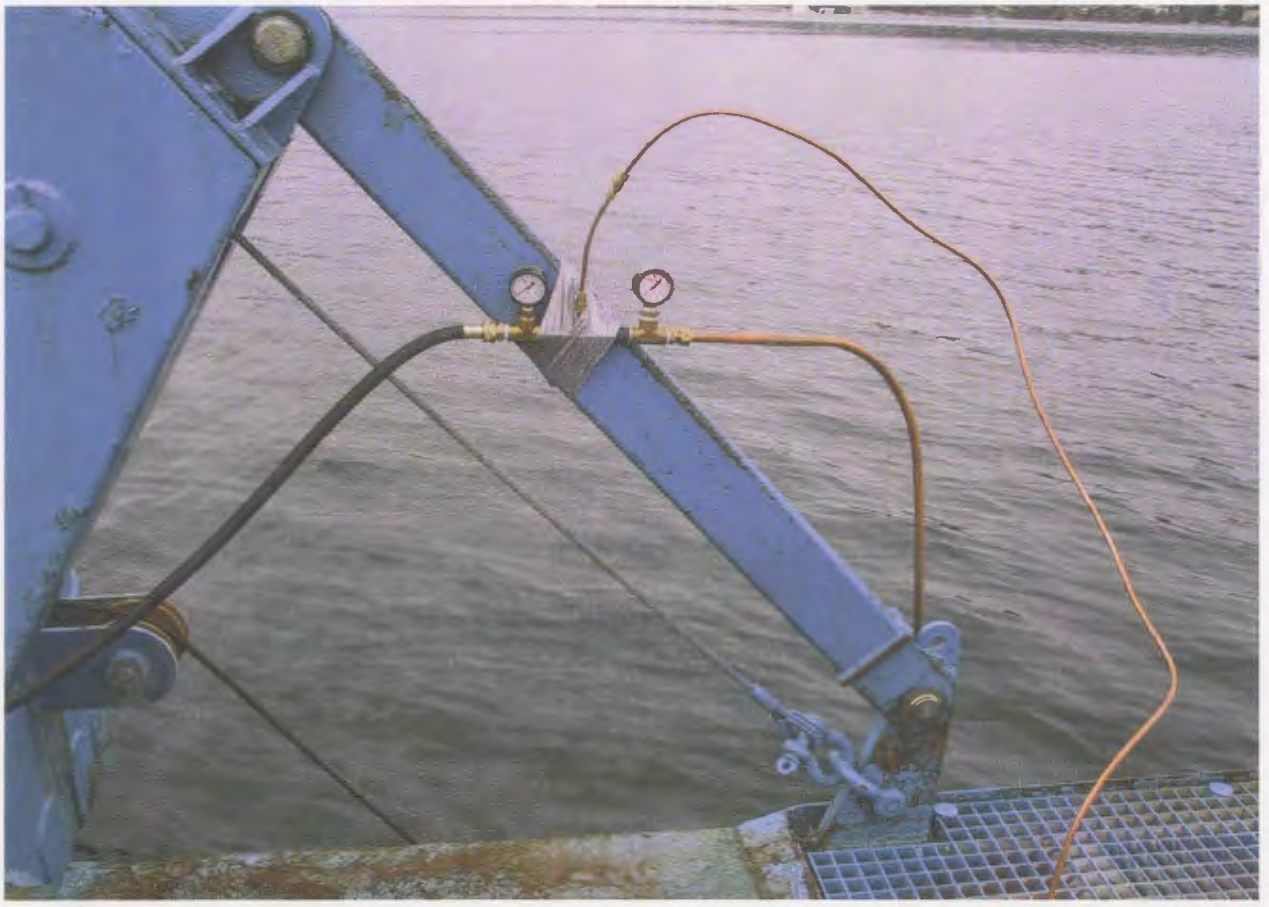

Figure 3-10: Tracer Dispensing Setup

3.4.3 PROGRAMMING THE VEHICLE:

All setup for the ARCS vehicle was completed by the ISE support staff. This included programming the vehicle's mission, performing daily checks to ensure all systems of the AUV were functioning properly, and preparing and completing launch and recovery of the vehicle.

Mission programming and daily checks were performed from a control room aboard the *Researcher*. These checks were used to ensure that all systems of ARCS were functioning correctly before each deployment. Examples of the systems checked were the power system and the navigation system. The control room is shown in Figure 3-11.

Figure 3-11: ARCS Control Room on *Researcher*

The control team had the ability to control ARCS during the mission through a radio link. The receiver for ARCS was attached to a surfboard that was towed by ARCS during the mission. The board served two main purposes: a location for the radio receiver, and an indicator that the vehicle was in the water as a warning to other boaters in the area. The surfboard for ARCS is shown in Figure 3-12.

Figure 3-12: Surfboard Towed by ARCS During Sea Trials

The ISE support staff used a crane on the foredeck of the Researcher to both launch and recover ARCS. Figure 3-13 shows the launching of the ARCS vehicle.

Figure 3-13: Launch of the ARCS Vehicle

CHAPTER 4 RESULTS

4.1 SAMPLING VS. IN-SITU SENSORS

One of the goals of this project was to compare alternative ways of collecting environmental data using an AUV. It was determined that the two main ways of collecting environmental data are sampling and using in-situ sensors.

While on the CCGS Hudson research cruise, the author observed several sample collection techniques. An overview of the research cruise is given in Appendix A. There were a variety of techniques that were all easy to do. However, sample collection on an AUV can be difficult, due to the large amount of space needed to collect the correct volume for each sample. Most laboratories request a larger volume of sample to be

submitted than that used for the analysis. This allows the laboratory to sub sample. In addition, duplicates are required to ensure that sample methods are accurate. Space is restricted in an AUV and the large volume requirements for samples result in fewer samples being collected.

In addition to the large volumes, sample containers should be considered. Certain samples need to be collected in glass bottles, which are heavy and add weight to the AUV. For example, all hydrocarbon samples need to be collected in glass bottles, and these compounds would be important to measure with respect to offshore oil and gas industry discharges. The shape of the bottles may cause mounting difficulties in an AUV. There may be much wasted space between bottles. Certain samples need to have preservatives added, or need to be kept at specific temperatures, which is difficult to control underwater. Typical volumes and bottle types for water samples for various parameters are shown in Table 4-1(Whelan, 2000).

Table 4-1: Typical Volume and Bottle Requirements for Water Samples

Parameter	Sample Volume Requested	Required Sample Volume
Poly-aromatic Hydrocarbons	2x250 mL glass	1x250mL
Oil and Grease	2x1L	1x1L
Total Suspended Solids	500 mL plastic	100 mL
Trace Metals	50 mL	50mL
Mercury	100 mL	100 mL

Parameter	Sample Volume Requested	Actual Sample Volume Req'd	Bottle Type	Method of Analysis
Total Suspended Solids	500 mL	100 mL	500 mL plastic	Gravimetric
Arsenic	50 mL	50 mL	50 mL plastic	ICP-MS
Cadmium				ICP-MS
Chromium				ICP-MS
Cobalt				ICP-MS
Copper				ICP-MS
Iron				ICP-MS
Lead				ICP-MS
Manganese				ICP-MS
Nickel				ICP-MS
Zinc				ICP-MS
Mercury	100 mL	100 mL	100 mL glass	CVASS
Naphthalene	2x250mL	250mL	250mL glass	GC/MS
Perylene				GC/MS
1-Methylnaphthalene				GC/MS
2-Methylnaphthalene				GC/MS
Acenaphthylene				GC/MS
Acenaphthene				GC/MS
Fluorene				GC/MS
Phenanthrene				GC/MS
Anthracene				GC/MS
Fluoranthene				GC/MS
Pyrene				GC/MS
Benz(a)anthracene				GC/MS
Chrysene				GC/MS
Benzo(b)fluoranthene				GC/MS
Benzo(k)fluoranthene				GC/MS
Benzo(a)pyrene				GC/MS
Indeno(1,2,3-cd)pyrene				GC/MS
Dibenz(a,h)anthracene				GC/MS
Benzo(g,h,i)perylene				GC/MS
1-Chloronapthalene				GC/MS
2-Chloronapthalene				GC/MS
Oil & Grease	2x1L	1x1L	1 L glass	IR
Vegetable Oil & Grease				IR
Mineral Oil & Grease				IR

There are many in situ samplers available on the market for certain purposes. Two were used in this experiment: the Micro CTD and the In-Spectr from Applied Microsystems Ltd. Examples of other types of sensors are fluorometers that can measure fluorescence in the water column and which give an indication of the concentration of phytoplankton, transmissometers that measure the turbidity or presence of particles, and current sensors to measure ocean currents.

4.2 EQUIPMENT EVALUATION

Both pieces of analytical equipment used in this project were evaluated qualitatively. This included the ease of installation, ease of use, and effectiveness of data format.

4.2.1 AML MICRO-CTD

The Micro-CTD was easy to install. The Micro-CTD is approximately 880 grams, 280 mm in length and 50.3 mm in diameter (AML, 2001-spec sheet). A mounting bracket came with the CTD, which held the equipment in place. Due to its small size, the CTD was easily placed in its mounting block. A cable tie ensured that the CTD did not slip out of place. The CTD was also easy to set up and use. It was pre-calibrated by the Applied Microsystems laboratory and a software package allowed the on-ship user to easily prepare the CTD for deployment. After the mission, a cable from the CTD was plugged into the laptop computer and the software allowed the information to be downloaded

easily. The resulting data format was simple and could be opened into a spreadsheet program.

4.2.2 THE IN-SPECTR

The In-Spectr is 38.5 kg, 138 cm in length and 19 cm in diameter. Two people lifted it easily into the AUV. Specially designed mounting blocks held the equipment in place. A user-friendly software program was provided with the mass spectrometer allowing easy setup and use. It guides the user through the boot-up process for the mass spectrometer and outlines each step to prepare the mass spectrometer for deployment.

Data were easily downloaded from the mass spectrometer using a simple cable connection. The data were easy to read and could be opened in a spreadsheet program. The sample time was shown as "time into the trial". The preference would be that the time be shown as the actual time.

The In-Spectr is very sensitive to power. A diode system was installed to minimize power interruptions. The system provided a constant 24 V that allowed power to be switched from shore-power to ARCS-power without interruption. The diode automatically switched from either source, depending on which was available (AML, 2000-2002). This system was required, as even slight power interruptions cause the instrument to shut down, which required a complete re-boot. This became problematic when the ARCS battery powered the mass spectrometer. Any power surges in the ARCS battery caused

the mass spectrometer to shut-down. The addition of a back-up battery, to power the mass spectrometer, would alleviate this problem.

4.3 MISSION RESULTS- MASS SPECTROMETER DATA

The field component of this thesis took place over three days in three separate trials. Each of the trials was essentially conducted in the same manner. Three trials were performed to ensure better data quality. Trials such as these, using the equipment of choice, have not previously been performed. Therefore, the three trials included "room for error" and were used to increase the reliability of the experiment. There was a small time frame in which the ARCS vehicle could be used on each day. This was primarily due to the battery life of ARCS. A single long trial would not have been appropriate, therefore, the trials were divided over three days. Each trial has been considered a separate demonstration.

4.3.1 TRIAL 1 – FEBRUARY 4, 2002

There are no data available for the mass spectrometer on February 4, 2002. The potting in the underwater cable protector leaked causing the mass spectrometer to stop logging data. A picture of the potting that leaked is shown in Figure 4-1. The problem was corrected for the rest of the sea trials by drying the cables and re-sealing the container. The container was resealed using two coats of liquid neoprene, and then several layers of tape.

Figure 4-1: Leaky Potting Causing Mass Spectrometer Failure, February 4, 2002

4.3.2 TRIAL 2 – FEBRUARY 5, 2002

A software package called "TranspectorWare" was provided with the mass spectrometer. It was used to read the mass spectrometer data in its raw form. In the case where the mass spectrometer can remain connected to the computer (in the laboratory), this will show real time data.

Figure 4-2 shows a screen from this software. It is a sample of the raw mass spectrometer data from February 5, 2002 plotted against "sample number". There was one mass spectrometer sample taken every 4.25 seconds.

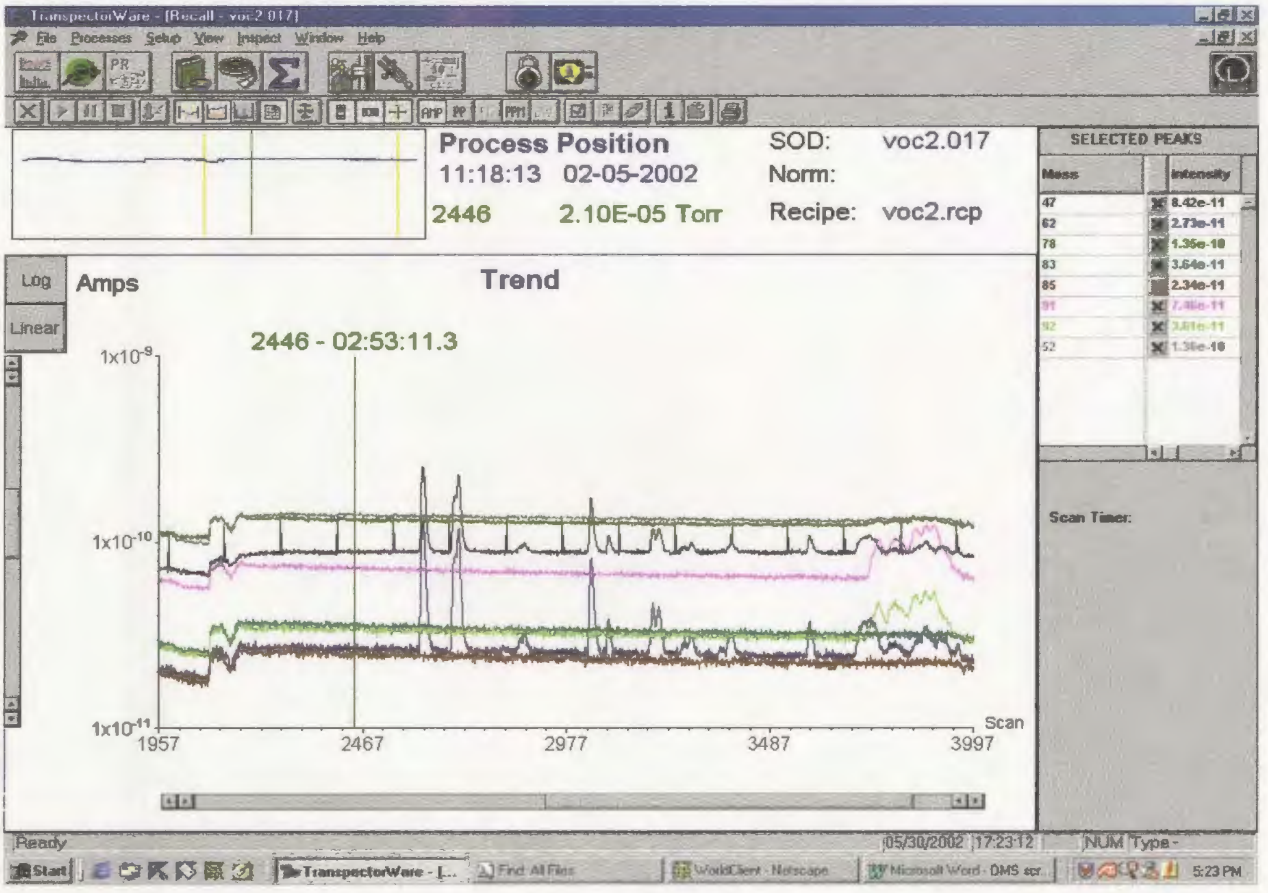

Figure 4-2: Raw Mass Spectrometer Data vs. Sample Number, February 5, 2002

The axes on the figure represent the scan number and the current. The scan number is essentially a measure of time, while the current is an indication of the presence of the chemical. The current is what the quadrupole analyzer measures once the separation of ions has taken place. Note that the measured current is small, in the order of 10^{-10} Amps.

Each of the five lines of colour indicates a different diagnostic ion that represents the presence of different chemicals in the water system. DMS is represented by the presence of two diagnostic ions, which are 47 and 62 (black and blue). The other diagnostic ions represent the following: toluene (91-pink, 92-green), chloroform (83-cyan, 85-brown), and benzene (78- dark green). The term "diagnostic ion" means that this mass to charge (m/z) value is a major peak in the mass spectrum of the compound of interest. In other words, if the compound is present, then you should see a peak at this m/z value. On the other hand, a peak at this m/z value does not necessarily mean that the compound is present, as there may be other compounds that give you a peak at the same m/z value. For this reason, a chemical with multiple diagnostic ions should have the equivalent number of peaks present for each ion in order to confirm that it is in fact the chemical in question. For example, in Figure 4-2, the sharp peaks occurring only in the black line are noise, and do not indicate the presence of DMS. Since the charge on the ions using electron impact ionization is almost always +1, m/z can usually be replaced by m or mass. In the case of dimethyl sulphide, with chemical formula $2(CH_3)S$, the mass is 62. However, DMS also exists as methyl sulphide, with chemical formula CH_3S, which corresponds to a mass of 47, the second diagnostic ion.

The start of the peak shows the time when the chemical becomes present in the sample stream. There are several DMS peaks shown in this sample. The largest two occur at sample times 2606 and 2683. There is also a single peak present for toluene. This was at the end of the mission, and occurs at a time when the AUV was near the ship engine. It is the only toluene peak present in the data and it is believed that it was attributed to the

ship's exhaust. It starts at sample number 3800. There were no other peaks for any other chemical.

4.3.2.1 Discussion of Data Interpretation

The data for DMS, from the mass spectrometer, were isolated and plotted against the position of the ARCS vehicle, using a MATLAB program. In order to get location data for the mass spectrometer several steps of data manipulation were used. As time is the only common factor in the mass spectrometer and ARCS data sets, this manipulation was performed to match the sample times, and as a result to provide positioning data for the mass spectrometer.

The ARCS navigation system and the In-Spectr were logging data at different rates and independently of each other. The navigation data for ARCS was being logged at a rate of about 9 samples per second, whereas the mass spectrometer was logging data only once every 4.25 seconds. The steps taken to manipulate the data, in order to match sample times, are described in the following paragraphs.

The first step required was to synchronize the clocks of the mass spectrometer and the ARCS vehicle. There was a one-minute time lag in the mass spectrometer between the time that the sample was collected and the time that the sample was analyzed. In addition to this, the mass spectrometer clock was two seconds ahead of the ARCS clock. As the interest was where the sample was collected, not analyzed, all of the mass spectrometer times were shifted 58 seconds ahead of the time actually recorded. For example, on Day

2, the mass spectrometer start time was recorded as 11:18:13. Taking into consideration the 58-second time shift, this was an equivalent ARCS time of 11:17:15. The corrected time was used as the standard.

The second step of the data manipulation was to ensure that the start and finish times for the two sets of data were the same. The start times recorded on each of the computers were different, as they were not necessarily turned on at the same time. For example, the start time of the mass spectrometer was recorded when the computer was disconnected from the land power source, which was about an hour before the vehicle was submerged in the water. The equipment did not stop recording until about 20 minutes after the vehicle was brought on board the ship. However, the start time required for analysis was the moment when ARCS was put into the water and the finish time was taken to be the end of the mission, before recovery. These times were recorded during the sea trials. All data stored before ARCS was submerged and after the mission was complete were removed from the analysis.

The ARCS navigation data were recorded at a rate of approximately 9 samples per second. The third step was to remove every ninth data point to get an even number of data points per second. It was assumed that the remaining eight samples per second were evenly spread. That is, it was assumed that one sample was collected every 0.125 seconds. The Matlab program code for this procedure can be found in Appendix C.

The fourth step was to save every 34th data point from the remaining ARCS sample log. An interval of 34 data points represented every 4.25 seconds, which was the sample rate of the mass spectrometer.

There was some error associated with this procedure. Mainly, the sample rate for ARCS was not exactly 9 samples per second. A new data file was created for every 10000 points recorded by ARCS. In some instances an extra point was lost or created during this switch. As a result, after the fourth step of manipulation there were 24 data points too many for the ARCS vehicle. It was decided to remove these points over the entire number of samples to reduce the error. Therefore, each 69th point was removed. This was the fifth and final step of data manipulation. Once complete there were exactly 1661 data points for both the ARCS and mass spectrometer. After all the time manipulation, the mass spectrometer time was still shown as "time into the trial" as opposed to the actual time. For consistency, the mass spectrometer time was converted to actual time using a Matlab program. The Matlab code for steps 4 and 5, as well as the time conversion, can be found in Appendix C.

4.3.2.2 ERROR ANALYSIS

The condensed mass spectrometer data for February 5, 2002 can be found on the disk in Appendix D. To get an estimate of the error in the data reduction method, the mass spectrometer time was graphed with the ARCS time, against sample number, and is shown in Figure 4-3. If the two times are equal, then the corresponding location data can

be considered accurate. The equations for both lines are shown as well. As shown, the equations are close.

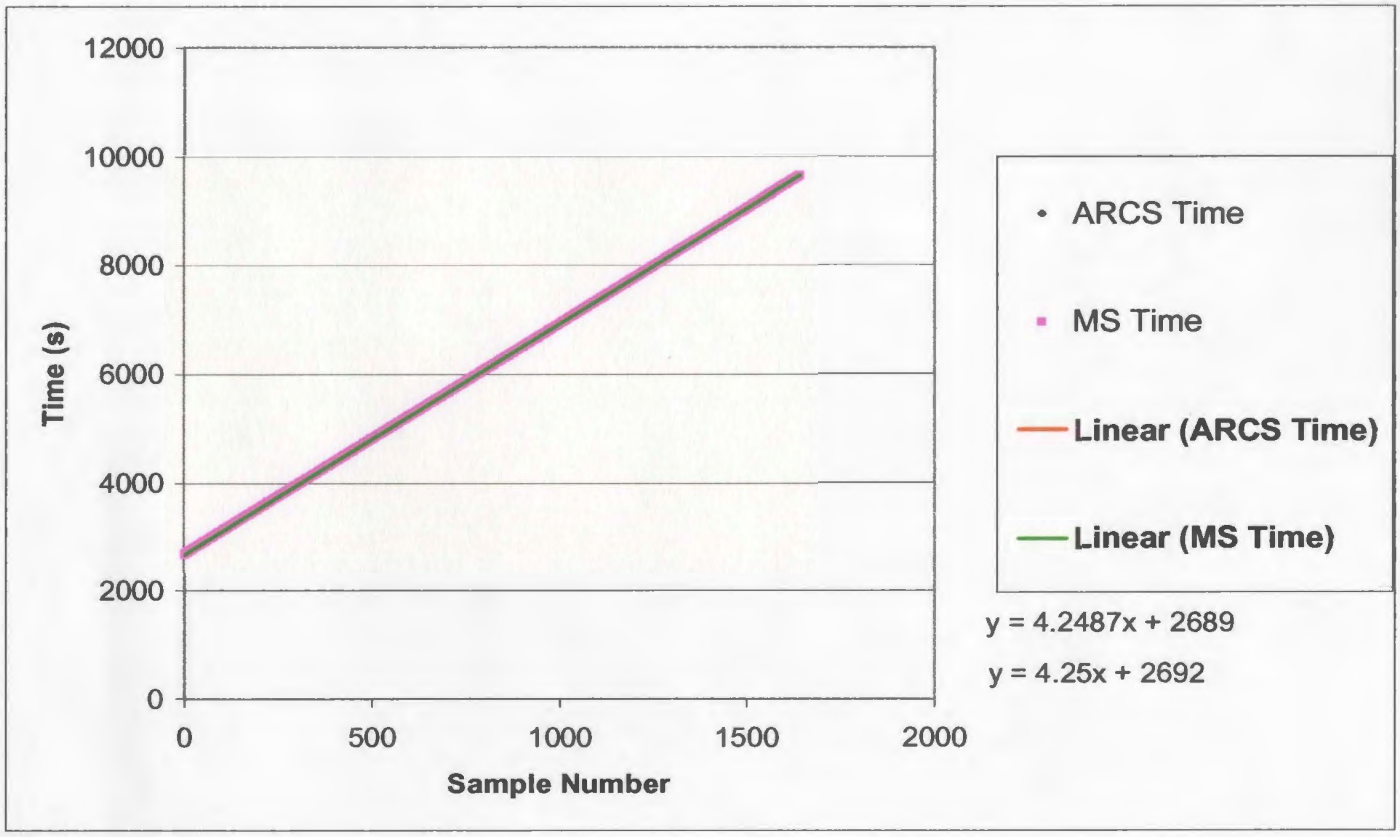

Figure 4-3: Error Estimate: MS and ARCS Time vs. Sample Number, Feb. 5, 2002

In addition, an estimate of the maximum error was calculated. The maximum error in distance was considered to be the product of the maximum time difference and the maximum speed of the ARCS vehicle. The maximum time difference between the ARCS vehicle and the mass spectrometer using the above method of data manipulation on February 5 was 7.5 s. The maximum speed of the ARCS vehicle was approximately 1.8 m/s. This resulted in a maximum error of 13.5 m. Essentially, this means that the position of the DMS samples are accurate to ± 13.5 m.

The average time difference and standard deviation were also calculated. The average time difference was 4.1 s, with a standard deviation of 1.4. These calculations are in the file containing the condensed mass spectrometer data, in Appendix D.

There is another source of error present in the determination of mass spectrometer location for all days. That is, the Internal Navigation Unit (INU) of the ARCS vehicle drifts from actual location. The actual drift is unknown, however, it is estimated that this total drift is less than 5% of the distance traveled (ISE, 2000-2002).

4.3.2.3 Data Plots

Figure 4-4 is a bird's-eye view of the ARCS mission. The diamond on the figure represents the anchor location for the Researcher. Essentially the figure shows the anchor location of the Researcher as well as the pattern that ARCS took through the water on the second day of sampling. The depth of ARCS during the trials was about 4 m. The ISE support staff pre-determined the path for ARCS before the mission with input from the captain of the *Researcher*. It was a typical AUV path, and the same that was used during the ARCS preliminary trials. The line indicates the path that ARCS took during the mission. The ship location is shown at the origin of the graph, and the ARCS path is shown as a distance in meters from the ship. ARCS completed its path three times during its mission. It was estimated, during the mission, that the DMS plume was located farther west than the original ARCS path, and it was assumed that it was too dilute near the most southern portion of the path. For this reason, the ISE support crew temporarily overrode

the autonomous mission and shifted the AUV path, first west, and then north. The vehicle was then restored to autonomous mode. For this reason, the three AUV paths do not overlay each other.

Positioning data from the ARCS vehicle were recorded as latitude and longitude. In order to convert these measurements to distance, the following equations were used:

$$Distance_x = (latitude_{ship} - latitude_{ARCS}) * 111216;$$

$$Distance_y = (longitude_{ship} - longitude_{ARCS}) * 72731;$$

where 111216 and 72731 are the distances, in metres, between two degrees of latitude and longitude respectively (Federation of American Scientists, 2003). The curvature of the earth was not taken into account, as it was negligible over the distance that ARCS traveled.

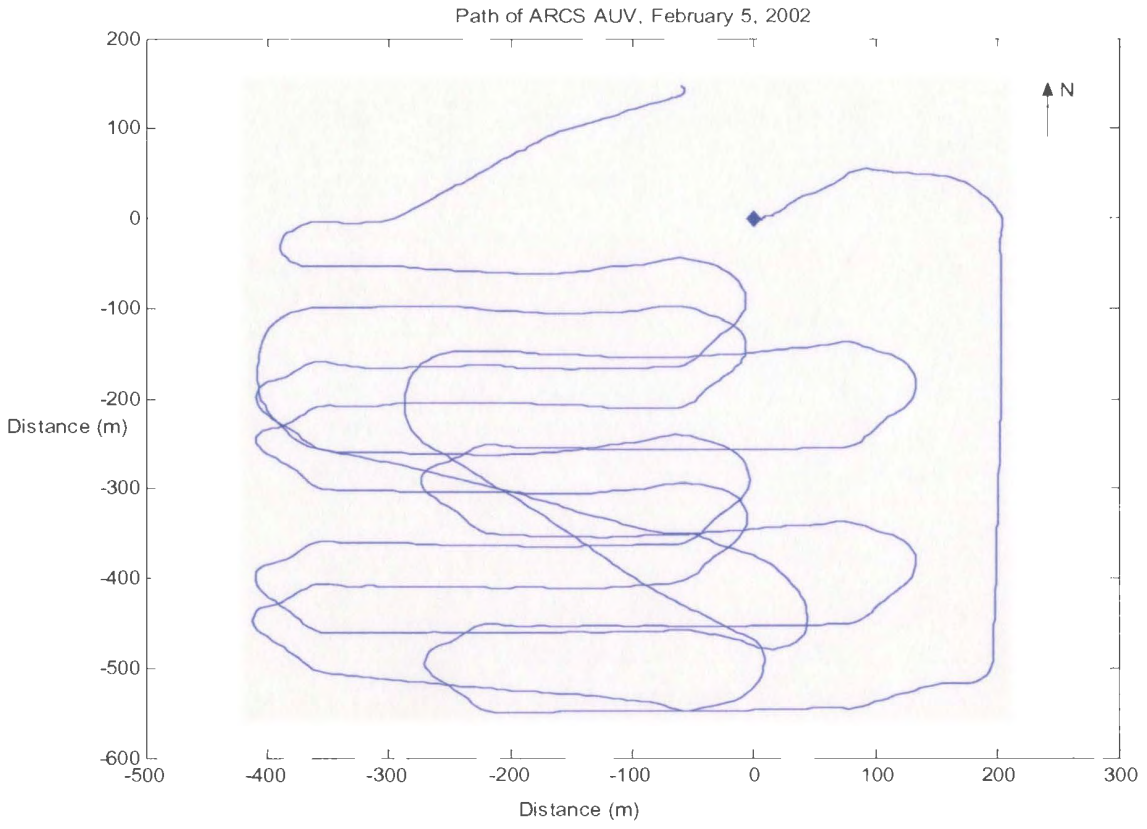

Figure 4-4: Path of ARCS AUV, February 5, 2002

In order to determine the location of the DMS plume, both indicator masses for the chemical had to be analyzed. The mass spectrometer data for diagnostic ions 47 and 62 were plotted in Figure 4-5. As discussed previously, a peak must be present in both masses in order to represent the detection of dimethyl sulphide. As shown in Figure 4-5, there is a lot of noise present in the mass 47 tracer, however less noise in the mass 62 tracer. Also, it was determined, visually, that in this case, the diagnostic ion 62 on its own was a good representation of the DMS. All peaks shown in the diagnostic ion 62 are present in the diagnostic ion 47, although the converse is not true. For this reason, mass 62 was used to represent the indication of dimethyl sulphide.

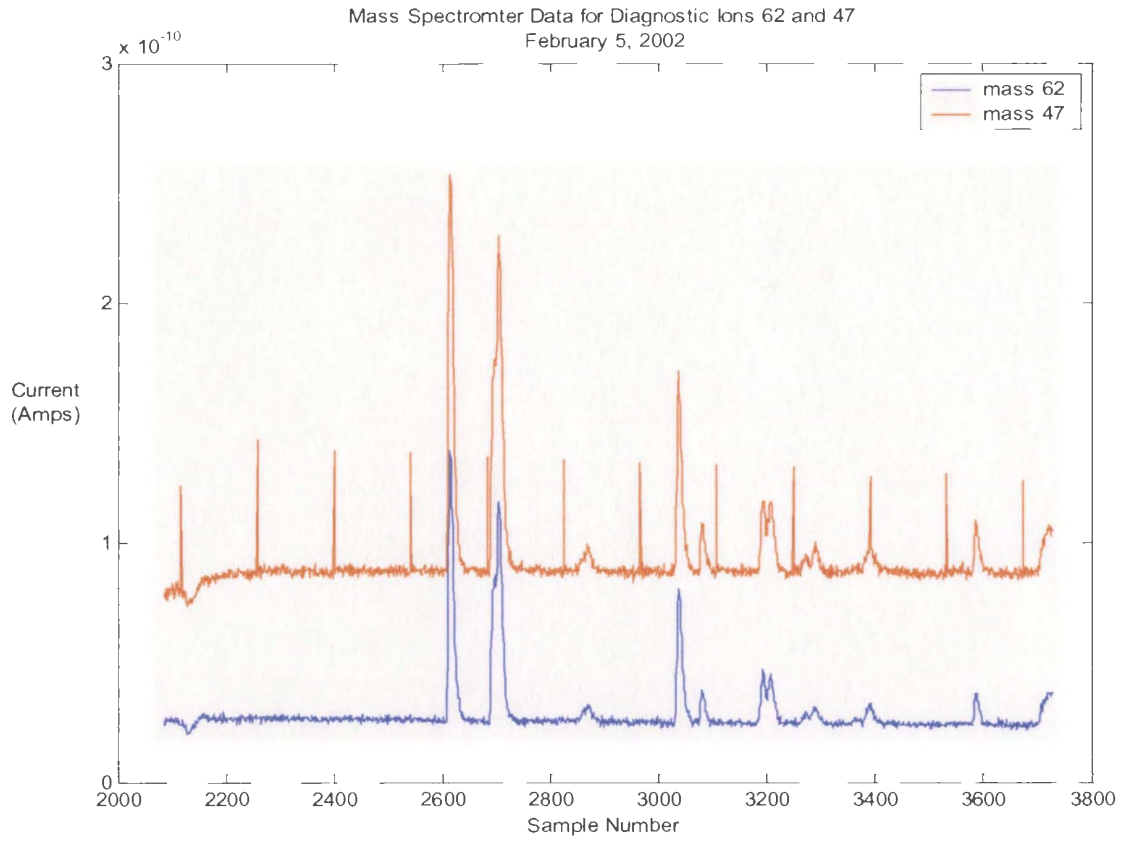

Figure 4-5: Mass Spectrometer Data for Diagnostic Ions 62 & 47, February 5, 2002

When analyzing the mass spectrometer data, it is important to understand the meaning of the peaks present. The start of the peak is representative of the time that the mass spectrometer first detected DMS, while the top of the peak is the time that the mass spectrometer stopped detecting DMS. The distance traveled between these two times is essentially the width of the plume at that location.

The data for the diagnostic ion 62 was isolated and thresholded to capture the peaks, that is, only the data that indicated the presence of DMS. A threshold value of 3.0E-11 was

chosen. To determine the location of the dimethyl sulphide plume, the data for the increasing portion of the peaks was captured using a Matlab program. The code can be found in Appendix C.

Figure 4-6 shows the location of the DMS with respect to the ship. The ship location and path are shown again as in Figure 4-4, and the DMS is represented by "x" markers on the line. As shown, the DMS concentration is located Southwest of the *Researcher*. This was expected as the current was in a southwest direction and was the main carrier of DMS through the inlet. As the DMS is found in the expected area it was deduced that the mass spectrometer did detect the DMS plume. The DMS is located in several small sets. Each set gives an indication of the width of the plume at that location. However, this width is not exact and there are gaps within each set. These gaps can be attributed to a variety of factors. Although there is no way to really quantify these factors, a qualitative discussion is provided.

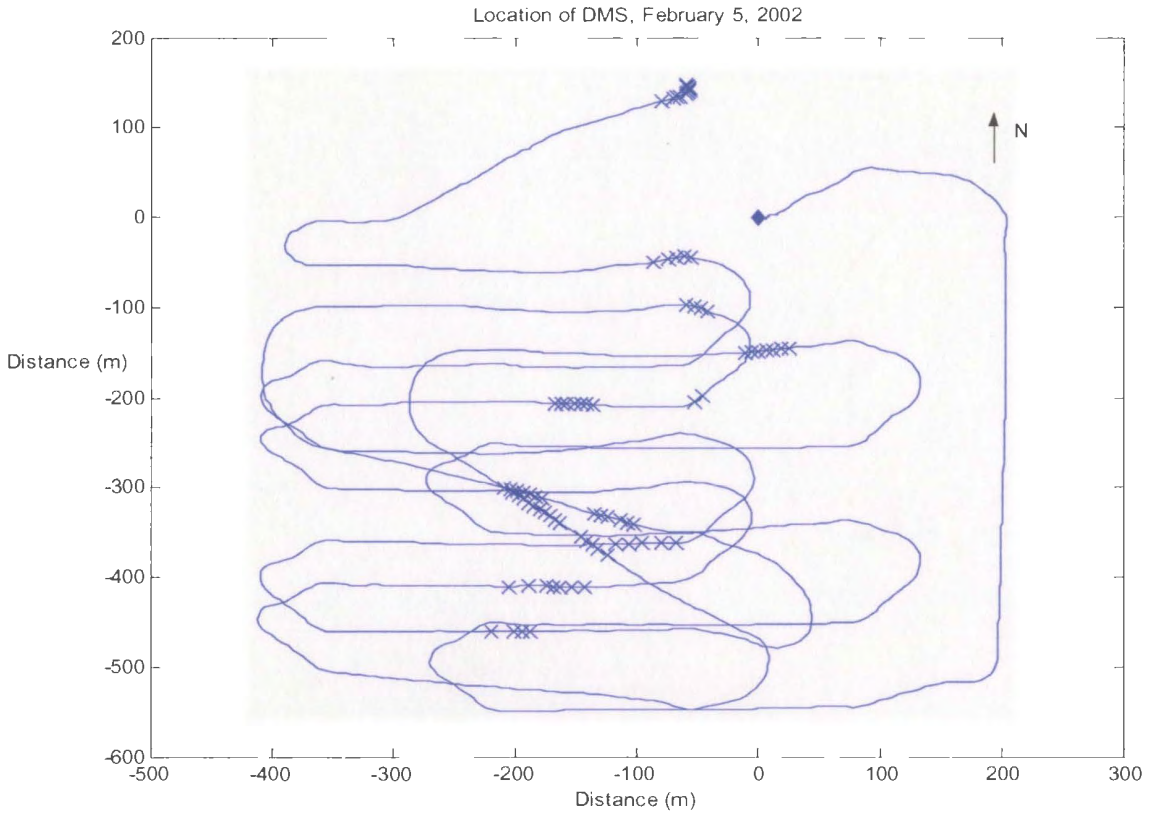

Figure 4-6: Location of DMS, February 5, 2002

The plume is relatively small in size and concentration, and natural changes such as eddies and current would likely affect the movement of the DMS. Depth changes with the AUV may also have contributed to missing data. Although the ARCS vehicle was programmed to have a constant depth of about 4 meters, hydrodynamic factors force the depth of the vehicle to vary. Another reason that gaps in the data may be present is due to the analysis process. As discussed, the increasing portion of the DMS peaks was isolated to determine the plume location. However, although the trend of the line was increasing, there were minor fluctuations of the current up and down. These minor downward fluctuations were lost as a result of the programming code.

It is shown that ARCS did, in fact, maneuver in and out of the DMS plume, indicating that the type of equipment used is valuable for plume delineation. One discrepancy exists with the DMS data. In the figure, a small amount of DMS is shown to be Northwest of the *Researcher*. This discrepancy is attributed to the navigation system on the ARCS vehicle. As shown in both Figure 4-4 and Figure 4-6, the ARCS path veers sharply north. This was at the point when the ARCS vehicle returned to the surface after completing its mission. In fact, the AUV was enroute to the Researcher and never went that far North. The positioning data after the sharp curve is inaccurate and is attributed to INU drift. In fact, the AUV was actually next to the ship at the time that the navigation system reported it as being the farthest point north.

4.3.3 TRIAL 3 – FEBRUARY 6, 2002

Figure 4-7 shows a sample TranspectorWare screen of the raw data collected on February 6, 2002. In the sample shown, there are several DMS peaks present. Although there are several peaks present, there are two DMS peaks that are more prominent than the others. One starts at sample number 2475 and the other starts at 2664. There are also two peaks present for toluene. This was at the end of the mission, and occurs at times when the AUV was near the ship engine. It is believed that these peaks are attributed to the ship's exhaust. The large peak starts at sample number 2670 and the smaller peak starts at 2817. There were no other peaks for any other chemical.

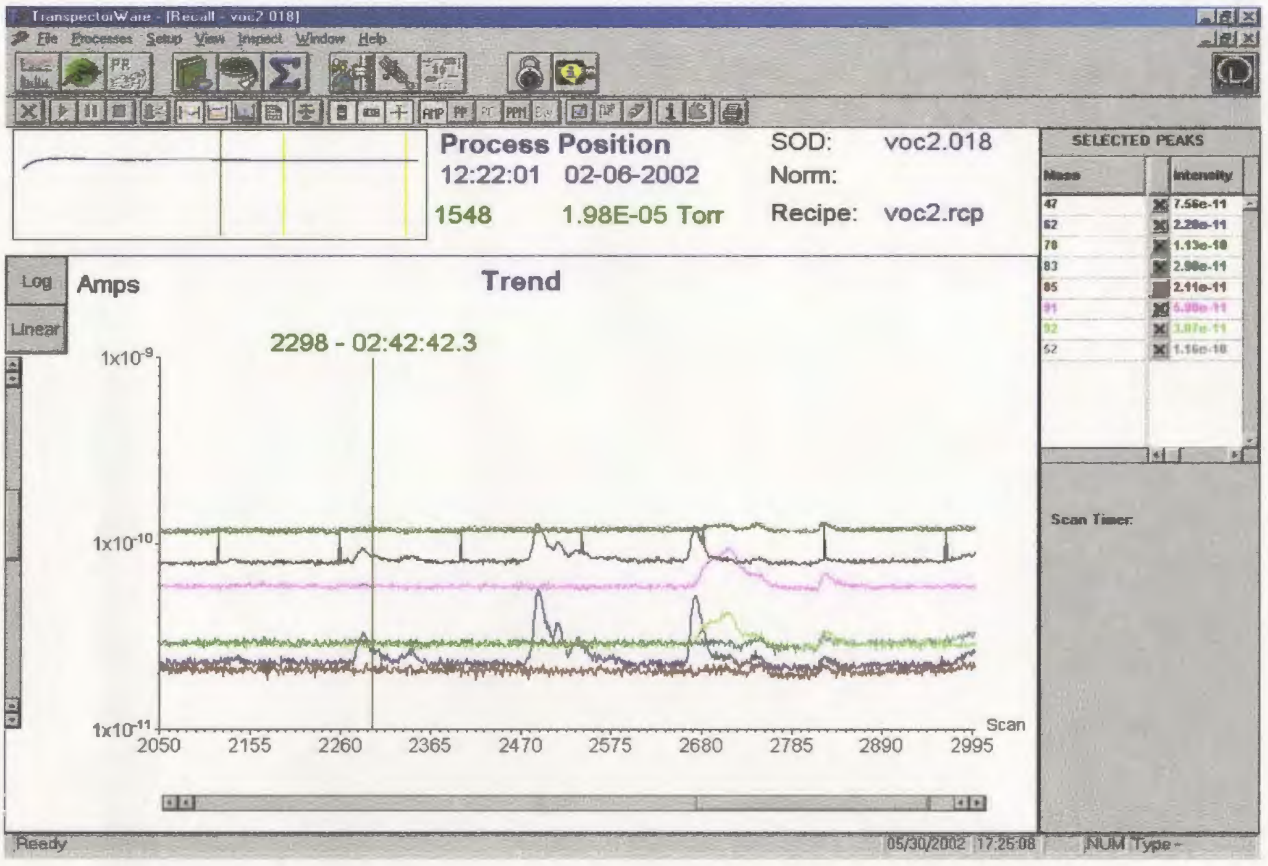

Figure 4-7: Raw Mass Spectrometer Data vs. Sample Number, February 6, 2002

4.3.3.1 ERROR ANALYSIS

The same process of data manipulation used in Trial 2 was used for the data from Trial 3 and it was previously described.

The condensed mass spectrometer data for February 6 can be found on the disk in Appendix D. To get an estimate of the error in the data reduction method, the mass spectrometer time was graphed with the ARCS time, against sample number, and is

shown in Figure 4-8. If the two times are equal, then the corresponding location data can be considered accurate. The equations for both lines are shown as well. As shown, the equations are close.

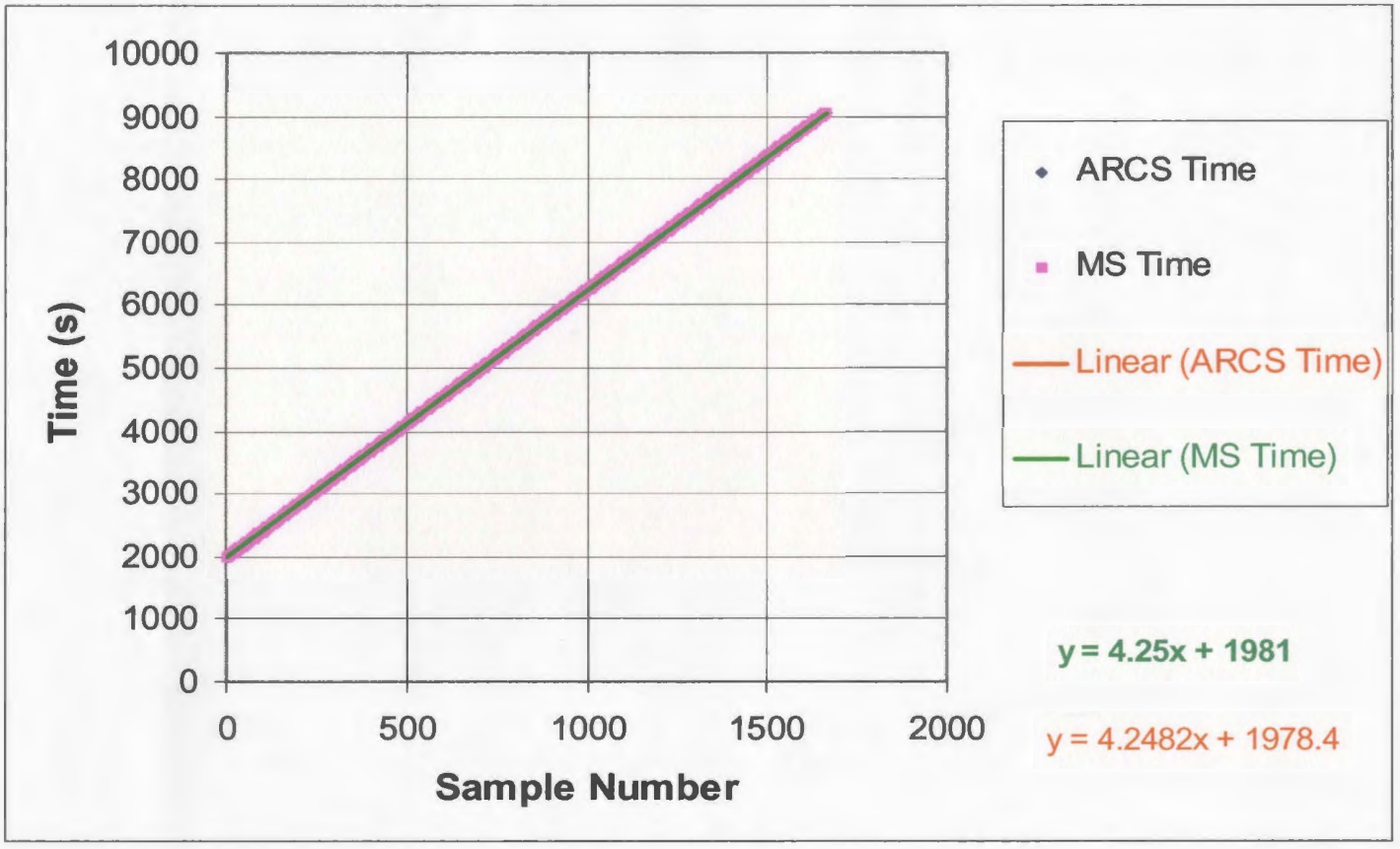

Figure 4-8: Error Estimate: MS and ARCS Time vs. Sample Number, Feb. 6, 2002

As in Trial 2, an estimate of the maximum error for the data manipulation for Trial 3 was calculated. The maximum time difference between the ARCS vehicle and the mass spectrometer using the above method of data manipulation on February 6 was 7.8 s. The maximum speed of the ARCS vehicle was approximately 1.8 m/s. This resulted in a

maximum error of 14.0 m. The average time difference and standard deviation were also calculated. The average time difference was 4.1 s, with a standard deviation of 1.5.

4.3.3.2 Data Plots

Figure 4-9 is a plan view of the ARCS mission. The diamond on the figure represents the anchor location for the Researcher on February 6, 2002. The figure shows the anchor location of the Researcher as well as the pattern that ARCS took through the water. The depth of ARCS during the trials was about 4 m. The path choice was similar to that taken on the previous day. Before starting the actual mission, the ARCS vehicle was piloted, from the control room, to a loop North of the Researcher. This was to ensure that there was no background DMS present in the inlet. The pass around the ship was made before any DMS was dispersed in the water. Again, the ship location is shown at the origin of the graph, and the ARCS path is shown as a distance in meters from the ship. The positioning data for ARCS was converted from latitude and longitude as previously described.

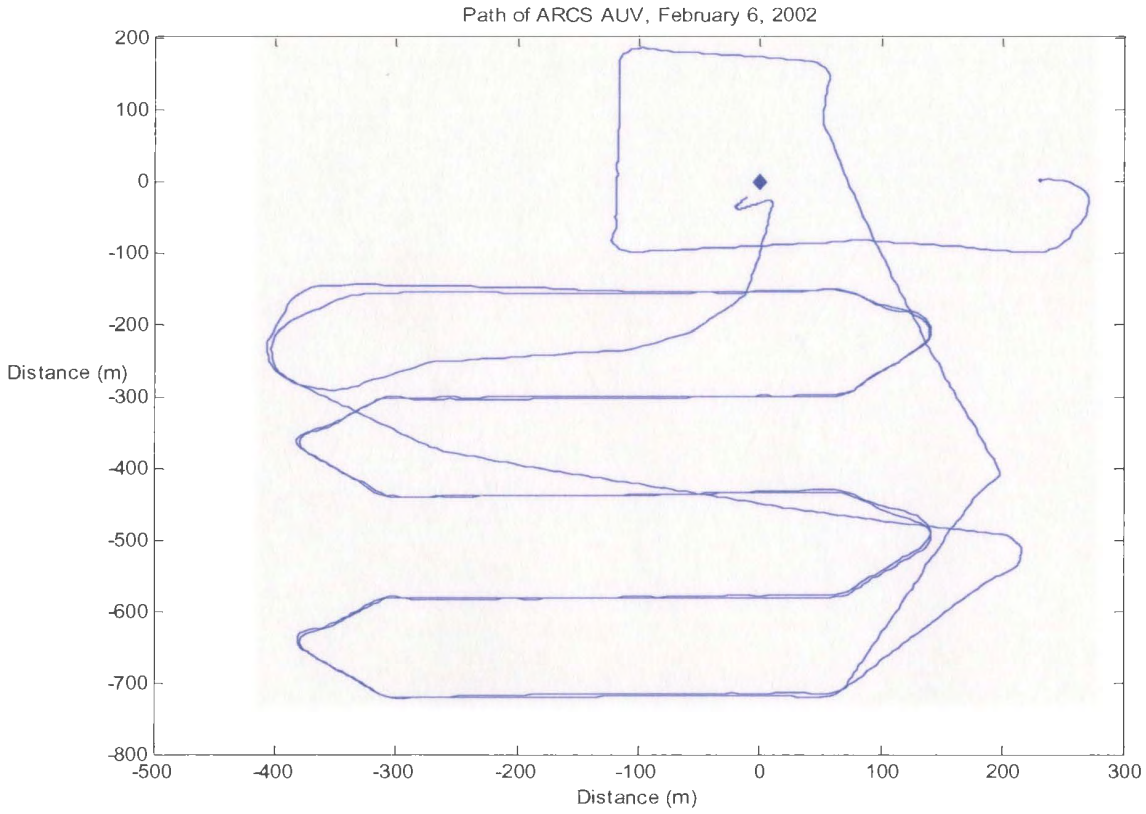

Figure 4-9: Path of ARCS AUV, February 6, 2002

The DMS data were visually inspected and it was determined that diagnostic ion 62 was again, on its own, a good representation of the chemical concentration. This is shown in Figure 4-10. All peaks present in diagnostic ion 62 are repeated in diagnostic ion 47, although the converse is not true.

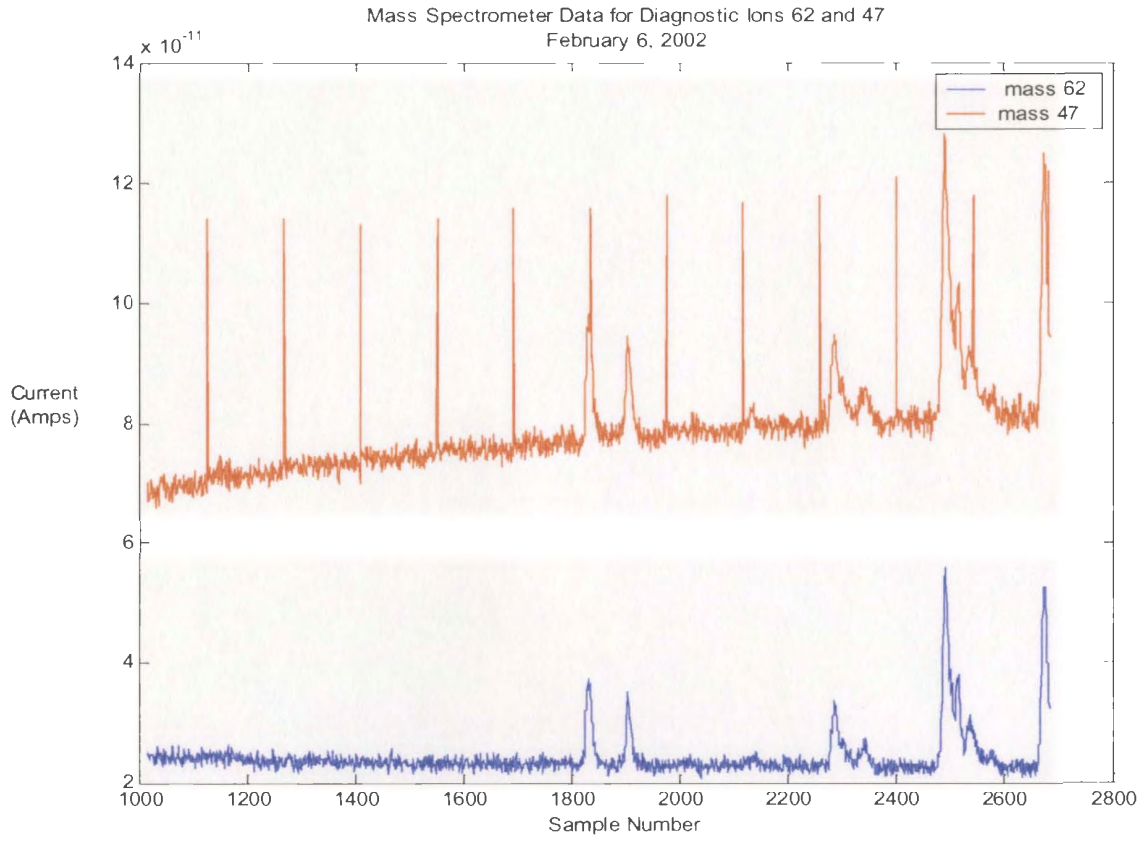

Figure 4-10: Mass Spectrometer Data for Diagnostic Ions 62 & 47, February 6, 2002

The DMS data for February 6, 2002 were isolated and thresholded in the same manner as previously described. The threshold was set at 2.65E-11 Amps. The location of the DMS plume was then determined by capturing the increasing portions of the peaks using a MATLAB™ code.

Figure 4-11 shows the location of the DMS with respect to the ship. The ship location and path are shown and the DMS is represented by "x" markers on the line. As shown, the DMS concentration was again found Southwest of the *Researcher*. No DMS was

found north of the ship, indicating that there was no background concentration. The north pass was made before DMS was dispersed in the inlet. The DMS on this day of testing was further west than before. This may have been attributed to environmental factors on the day such as changes in currents, or an increase in wind.

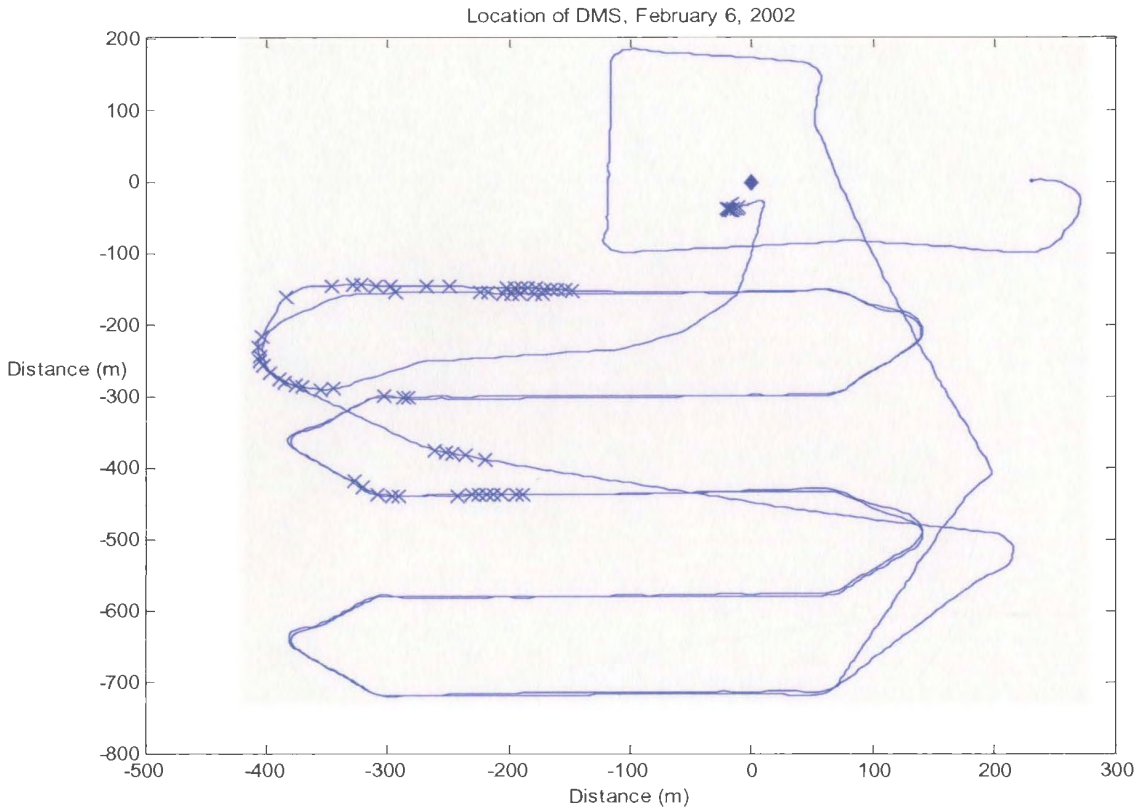

Figure 4-11: Location of DMS, February 6, 2002

4.4 MISSION RESULTS- MICRO-CTD DATA

Data for conductivity (salinity), temperature and depth were collected using the Applied Microsystems Micro CTD for all three days of field trials. Temperature was plotted against Time for all three days and is shown in Figure 4-12, Figure 4-13, and Figure 4-14. The temperature was relatively constant for all three trials. There is less than half a degree between the maximum and minimum temperatures for Trial 1, and just under a degree difference for Trials 2 and 3. The maximum temperatures on each day were recorded and were 7.658, 7.941, and 7.933 degrees Celsius respectively. The minimum temperatures for each day were 7.175, 7.232, and 6.971 degrees Celsius respectively. These temperatures are so accurate because the Micro-CTD can record temperature data to three decimal places.

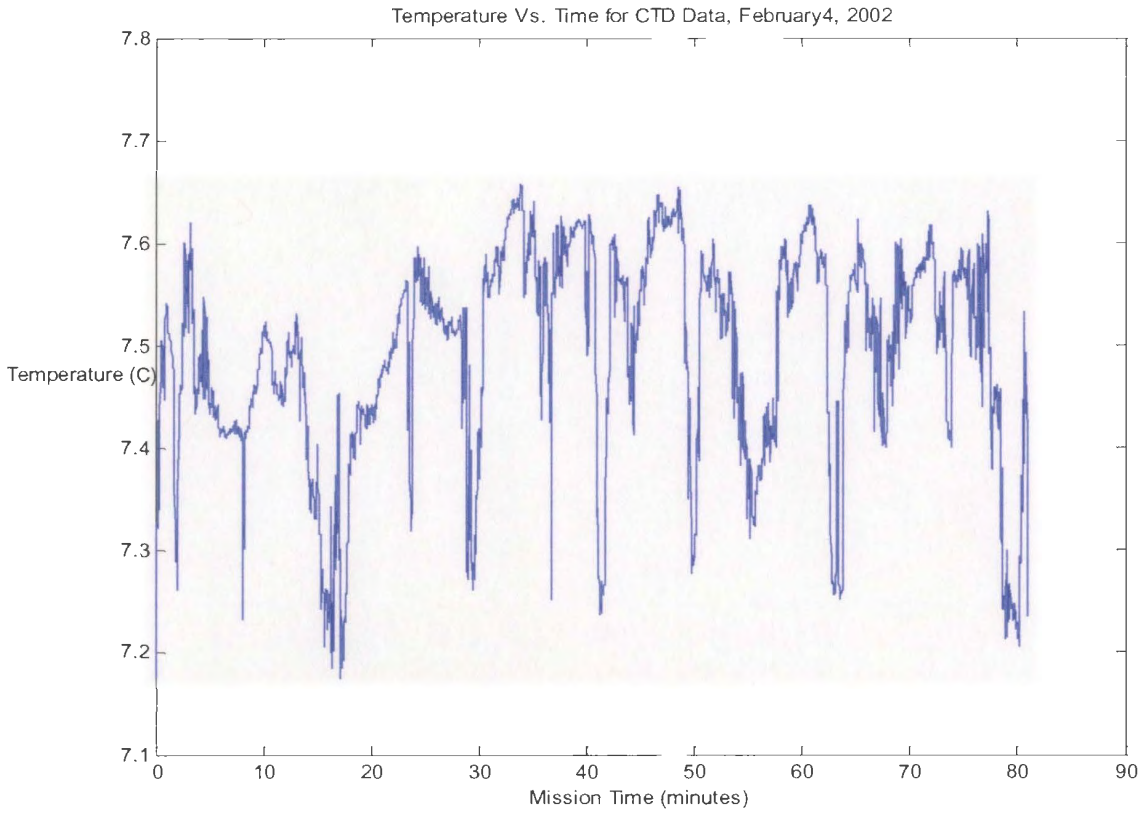

Figure 4-12: Temperature vs. Time for CTD Data, February 4, 2002

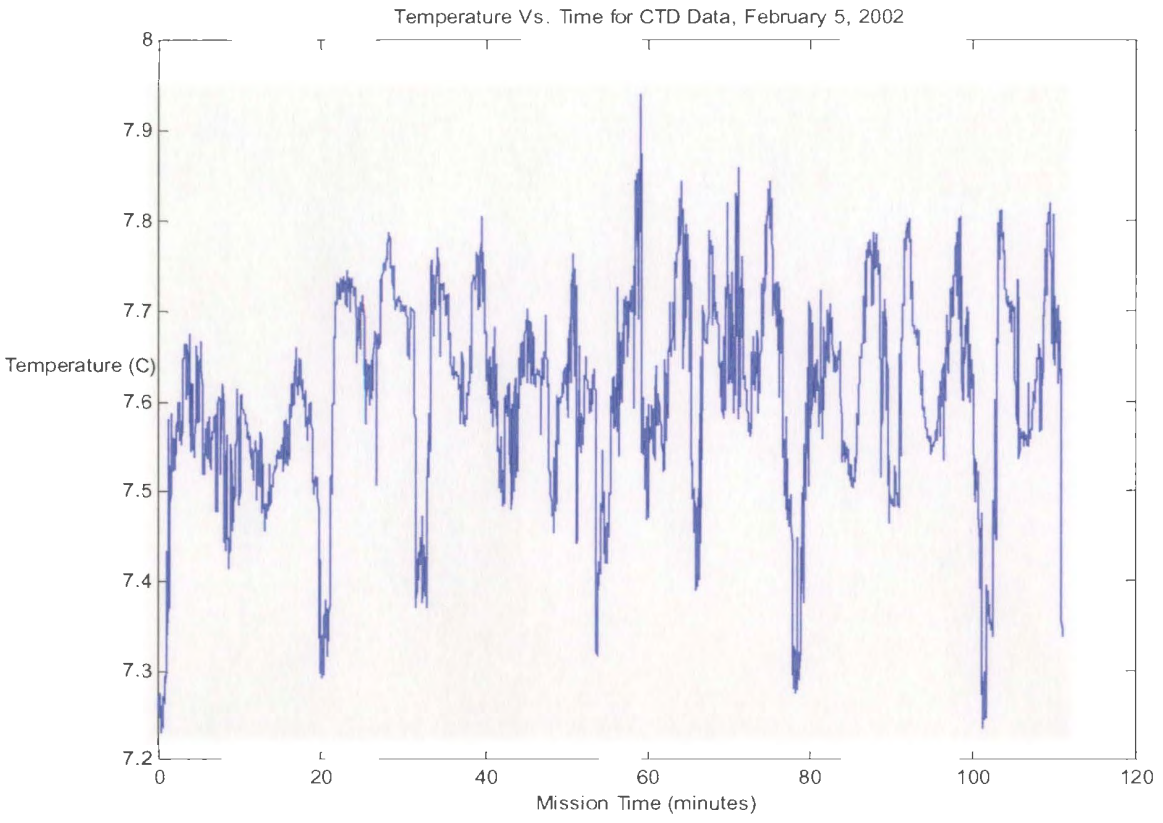

Figure 4-13: Temperature vs. Time for CTD Data, February 5, 2002

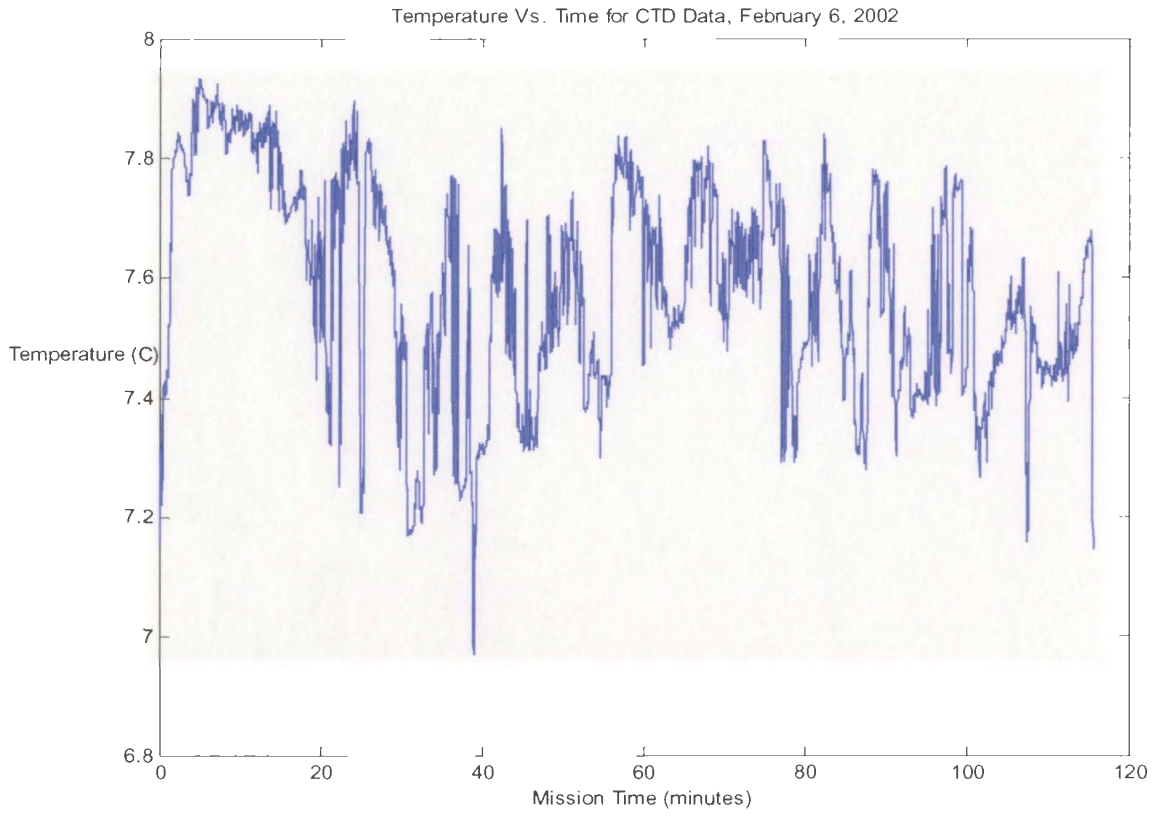

Figure 4-14: Temperature vs. Time for CTD Data, February 6, 2002

Salinity and pressure data were plotted against time for all three days of trials and are shown in Figure 4-15, Figure 4-16 and Figure 4-17. Pressure increases with depth, and therefore can be considered a measurement of the depth. Inversely, the pressure decreases, as the AUV approaches the surface. As shown in Figure 4-15, Figure 4-16 and Figure 4-17, salinity measurements were proportional to pressure measurements. The salinity decreased as the AUV approached the surface. This trend is due to the significant precipitation in the area during the winter months. The winter precipitation in Vancouver significantly lowers the salinity at the surface (Waldichuk, 1965). In fact, there was rainfall during the sea trials.

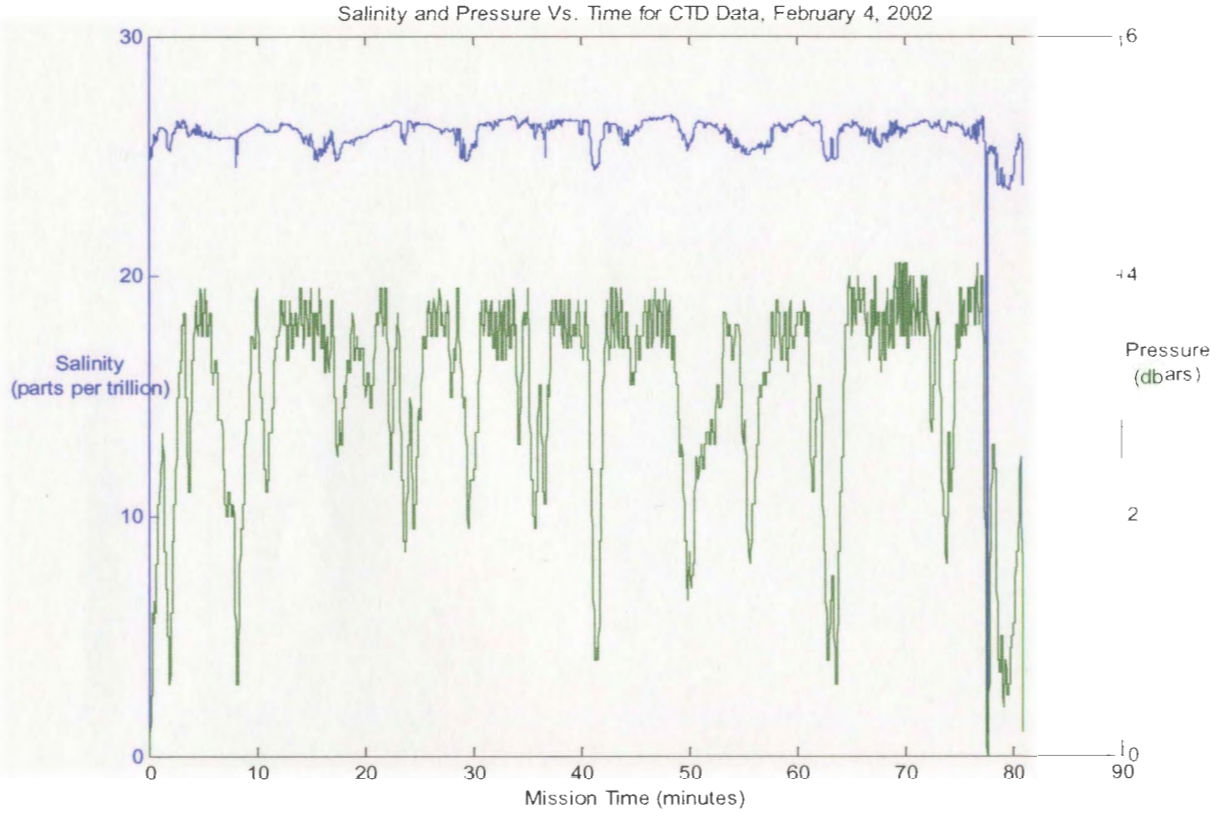

Figure 4-15: Salinity and Pressure vs. Time for CTD Data, February 4, 2002

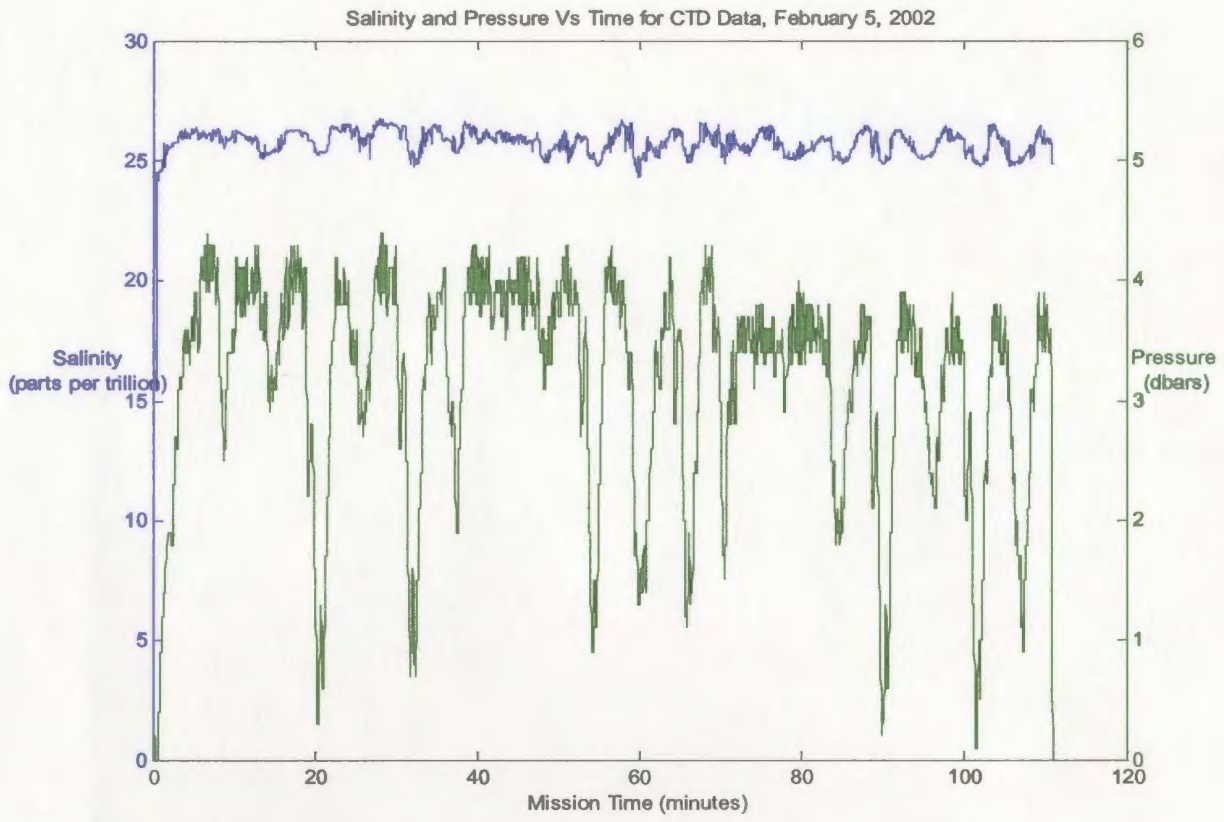

Figure 4-16: Salinity and Pressure vs. Time for CTD Data, February 5, 2002

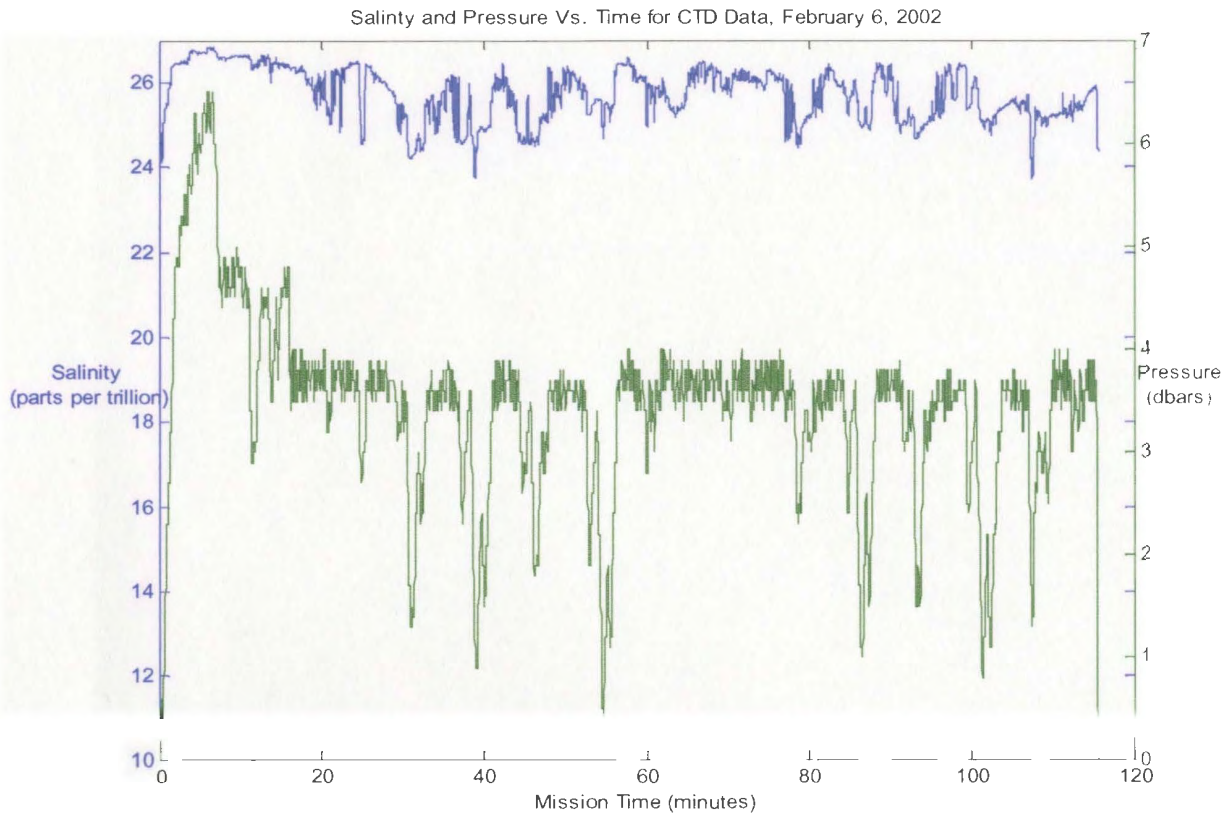

Figure 4-17: Salinity and Pressure vs. Time for CTD Data, February 6, 2002

CHAPTER 5 CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSIONS

This thesis has shown that an autonomous underwater vehicle can be used, with the correct analytical equipment, for environmental sampling. It was demonstrated that the payload package used for this deployment, consisting of the Applied Microsystems mass spectrometer (In-Spectr) and Micro-CTD, could be used for plume sampling and detection.

The Micro-CTD was considered most appropriate for the detection of thermal plumes or hydrothermal vents. However, it could be used, as in this deployment, to look for natural variations in temperature and salinity. The instrument was easy to use, and easy to

install. The software packages provided with each piece of equipment are user friendly and provide instructions for setting up and using the instruments. The installation was easily completed, as only simple clamps were required to keep the instrumentation in place. Its small size and mass make it an appropriate instrument for AUV use.

The In-Spectr was an effective tool for detecting a chemical in the water column. The results of the sea trials showed that the mass spectrometer, in conjunction with an AUV, was able to detect a chemical plume. The mass spectrometer could be used to detect any chemical plume, provided the chemical in question meets the constraints of the mass spectrometer. These constraints are that the chemical must be less than 200 atomic mass units, and relatively non-polar, or non-soluble in water. The mass spectrometer used in the deployment is also not appropriate for detecting metal concentrations. Other options for environmental monitoring of chemical falling into these constraints must be considered.

For this test, dimethyl sulphide was used. It is possible that the In-Spectr could provide the capability to detect certain chemicals within produced water plumes, such as hydrocarbons, although additional investigation would be required. The mass spectrometer tested does have the capability to detect certain hydrocarbons, mainly the lighter fraction hydrocarbons, for example toluene. It is unknown whether or not these chemicals are in high enough concentration within a produced water plume for the mass spectrometer to detect. Additional information would be required.

The continuous mode of sampling of the mass spectrometer was effective for determining plume location, as increases in concentration were shown. The same mode might be chosen when trying to verify an estimate of plume location. However, if this instrument was to be used for determining concentrations, the non-continuous mode should be used. For example the instrument might be considered for use in environmental regulation enforcement, to ensure that chemical concentrations are below required levels. For this type of analysis, a baseline concentration would be required.

Sample collection methods are not considered viable options for AUV use. Volume requirements are too large, resulting in an inadequate number of samples. In addition, AUV launch and recovery can be time consuming during trials, and continually bringing samples back to ship or shore is inefficient. In-situ sensors can be launched for extended periods of time, resulting in a greater amount of data. Also, the potential exists for real-time measurement if the AUV is capable of sending the data back to ship or shore.

There are several existing models for predictions of concentration and delineation of produced water plumes, however they lack real data and verification. An example of a model is the CORMIX model discussed in the thesis. An AUV with an appropriate sensor package could be used to validate these models. An instrument such as the In-Spectr could trace chemicals, for example hydrocarbons, in the produced water plume. This type of data would be valuable for use in long-term environmental effects monitoring. This is due to the fact that AUVs can be launched for extended periods of

time with continual data collection. It is important to consider new methods of environmental monitoring offshore, and AUVs can be considered a feasible option.

5.2 RECOMMENDATIONS

There were challenges faced during this thesis that need further consideration. Some may provide interesting research topics, while others are smaller items that would make field trials using this type of equipment more efficient. Several recommendations have been made as a result of these challenges and are as follows:

- Performing a field mission with the In-Spectr and an AUV using the non-continuous mode of sampling. It was determined in this thesis that the continuous mode is effective at determining plume location. A test investigating that non-continuous mode would complement the data from this thesis;
- Testing the payload offshore to determine its effectiveness for produced water monitoring. Lab tests of the mass spectrometer using samples of produced water would also be useful;
- Developing a complete feasibility study to compare the advantages and disadvantages of using an AUV vs. a ship for offshore monitoring;
- Synchronizing the clocks of ALL analytical equipment with the AUV before deployment. This would drastically reduce the time required for data manipulation. The time stamps would be ready for comparison upon download;
- Program the AUV to record a time stamp at the same rate as the mass spectrometer. The data manipulation process used to get the data in a useful form was time consuming. The AUV data needed to be reduced from over 100,000

samples to approximately 1650 samples. Two equal sample rates would ensure that data was ready for analysis as soon as it was downloaded;

- Providing a back-up power system for the In-Spectr that can ensure a reliable and continuous power supply in the face of temporary unforeseen interruptions; and
- Perform field trials with a different sensor package to investigate the uses of other sensors on an AUV, such as fluorometers and transmissometers.

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APPENDIX A:
Hudson Cruise Report, June 2000

Introduction

The Bedford Institute of Oceanography Cruise took place from June 11 to July 9, 2000 on the *CCGS Hudson*. The purpose of the cruise was to collect scientific data to be used in oceanographic research. The author took place in the cruise for the first leg from June 11 to June 25. Figure A-1 below shows the *Hudson*.

Figure A-1: CCGS Hudson

The main purposes of the first leg of the cruise were:

1. Test the redesigned Towcam, an instrument used to view the ocean floor;
2. Conduct surveys at the decommissioned Panuke platform to look for residual contamination from past produced water discharges and collect produced water samples from the active Thebaud platform;
3. Conduct conductivity, temperature, depth and nutrient samples from the Gully;
4. Collect environmental information on the distribution of drilling wastes around Hibernia;
5. Test shellfish moorings to measure the effects of drilling wastes and collect video-grab samples for benthic community analysis; and
6. Recover current meters at Hibernia.

While on the cruise, the author observed all the sampling equipment on board and participated in a regular scientific watch. A regular watch consisted of four hours on, and

eight hours off. The information in this report summarizes the daily activities of the scientific crew during the cruise.

Cruise Summary

June 11 – June 12

The first two days of the cruise were spent in the Bedford Basin, Nova Scotia. All equipment to be used on the cruise was tested in the basin successfully, with the exception of *Towcam*. Towcam is used to get a large view of the ocean floor. It is lowered into the water using a winch, and is towed behind the ship at a speed of about two knots. The video camera is connected to a monitor on board where the sea bottom can be viewed in real time. Unfortunately, Towcam failed the tests in the basin. The original Towcam was lost at sea during the cruise of 1999. Engineers tried to copy the old design, but upon testing, it was determined that the new Towcam was unstable and had a list of about seventy degrees in the water below speeds of about 4 knots. The Towcam design principle is similar to that of an airplane. The 'wings' and 'tail' allow it to fly smoothly in the water. Towcam should fly smoothly at speeds as low as 2 knots. Adjustments to the design were made, and Towcam finally flew correctly, however, the electrical component then failed. A decision was made to omit the Towcam trials from the cruise plan, and carry on. Towcam is shown in Figure A-2.

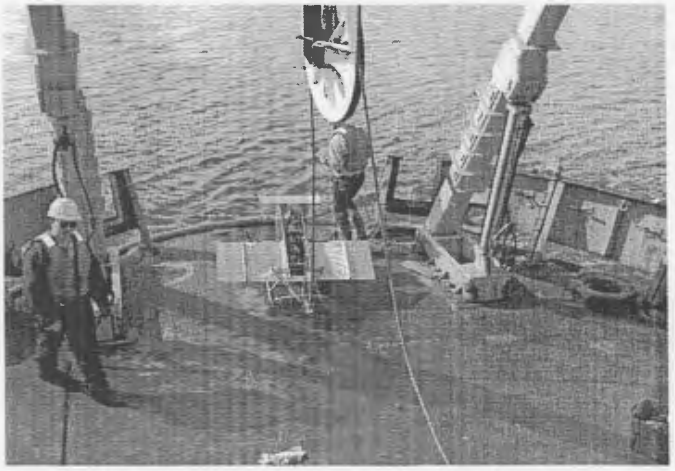


Figure A-2: Towcam

In addition to equipment testing, the first days were spent becoming familiar with ship procedures. This included a full fire drill and evacuation. The portside lifeboat was deployed and retrieved as part of this drill.

The *CCGS Hudson* departed Halifax at 21:00, June 12, 2000.

June 13

The *Hudson* arrived at the Panuke site at about 11:00 where samples were taken at six stations west of the platform. There were three platforms in view: Rowan Gorilla 3 (RG3), Rowan Gorilla 5 (RG5) and Panuke. Regular watches were started at this time. RG1 is shown on the horizon in Figure A-3 and Panuke is shown in Figure A-4. The Panuke picture was taken at a distance of about 50 m. The ship got very close due to the good weather.

Figure A-3: Rowan Gorilla 1

Figure A-4: Panuke

There were two different events performed at each station. The first event was the lowering of CTD (Conductivity, Temperature, and Depth). This piece of equipment was lowered into the water using a winch. A computer on board measured the three parameters on the way down. In addition to measuring these three parameters, CTD had the ability to store four water samples at various depths. Once CTD reached near-bottom, which was determined using navigation equipment on ship, the winch was stopped. Then, the first of four sample bottles was fired to activate sampling. Firing the bottles means initiating the process that forced CTD to collect samples. Computer equipment on board controlled the firing of the sample bottles. The winch then brought CTD slowly up to 50 m, where the second bottle was fired. This process was repeated at a depth of 25 m and at the surface. For this site, no water samples were taken. The CTD data was stored in a computer database. CTD is show in Figure A-5.

The second event was the lowering of BOB. BOB stands for "Brother of BOSS" where BOSS means Benthic Organic Sestonite Sampler. BOSS will be described in more detail later in the report. BOB contained five large syringes and worked on a timer. It was lowered into the water and onto the ocean floor where it remained for about a minute and a half. BOB fired the first syringe using the timer and this started the firing of the other four syringes. The samples were collected at small depth intervals, as the syringes were stacked two bottles high. The bottles collected 8 L of sample. In this case, the samples were analyzed in the on-board lab. Figure A- 6 shows BOB.

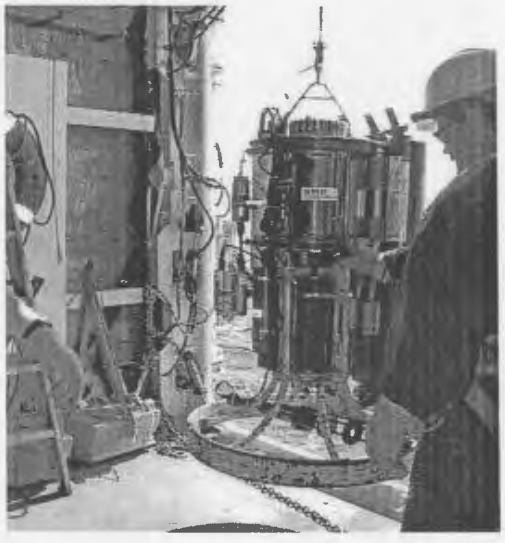


Figure A-5: CTD

Figure A-6: BOB

These two events were performed at each of the transect stations. After all of the western transect stations were complete, BOB samples were taken north, east and south of the platform. Once finished at the Panuke site, the *Hudson* steamed to the operating Thebaud platform. A produced water sample was taken directly from the platform. The sample that was collected was in the untreated state. The FRC (Fast Rescue Craft) of the *Hudson* was deployed, carrying five scientists and crew members. The FRC traveled to the platform where the produced water sample was collected. The sample was lowered from the platform into the FRC using a crane. In addition to the produced water sample, sea water samples were collected directly under the rig. A series of tests were to be performed on the samples at the labs in BIO in Nova Scotia. The samples were stored in a cold room for the remainder of the cruise.

The Thebaud platform is shown in Figure A-7.

Figure A-7: Thebaud Platform

During the night, the ship steamed through the Gully. During the steam, nutrient samples were collected. To collect the nutrient samples, a pumping system was placed in the ship and sea water was pumped through an intake to a hose in the forward lab. A small vial of sample and a duplicate were collected every ten minutes. These samples were

immediately frozen for testing upon return to BIO. A series of 14 CTD samples were also performed at the Gully. The water sampler on CTD was used at this site and the samples collected were used for testing nutrient and oxygen. The nutrient samples were frozen and stored, and the oxygen samples were tested immediately in an on board lab.

June 14

The 14th was spent steaming to Hibernia. The *Hudson* was expected to arrive ahead of schedule. A briefing schedule of the events to be held at Hibernia was held. This information session explained the procedure for getting the research underway upon arrival.

June 15

Steaming continued towards Hibernia. During the morning, while steaming, MIMS (Moored Impact Monitoring System) was prepared so that it could be deployed upon arrival at the site. MIMS looks much like a tripod and it is a mooring system, meaning that it is left in the water for an extended period of time. MIMS contained several devices. It had a current meter to measure local current. A transmissometer and an OBS (optical backscatter sensor) were mounted to measure turbidity, which is the amount of suspended particles. An altimeter to measure the changes in height of the seabed and sand waves was added, as well as a plankton silhouette to take a series of photos of plankton. All information gathered by MIMS is stored on a memory device (black box) until the mooring is brought back on board.

The *Hudson* arrived at Hibernia at 16:30. The science program for Hibernia commenced immediately upon arrival. First, MIMS was deployed Northeast of the GBS. It would later be picked up during the cruise. Figures A-9 and A-10 show Hibernia and MIMS respectively.

Figure A-9: Hibernia

Figure A-10: MIMS

At Hibernia, there were several transect stations, as well as three anchor stations. The transect stations were set at distances of 20, 10, 2, 1, 0.5 kilometers on various sides of the platform (N, S, E, W, NW). The events performed at the transect stations included Campod, CABLE, and CTD. CTD has previously been described.

CABLE is the Compact Aquatic Boundary Layer Explorer. It takes two water samples at the bottom and also contains a depth sensor, a camera and an OBS. For these stations, the water samples from CABLE were filtered to collect the sediment in the water. The

filter papers were then dried in a hot oven. The sediment samples were stored in the oven to be analyzed at a later date at BIO. The sediment samples will be analyzed for quantity as well as for their composition and grain size. Occasionally a water sample from CABLE was frozen to test for nutrients at a later date.

Campod is an underwater camera which takes still shots as well as video recording. Campod looks like a tripod and is controlled by a combination of manual and mechanical measures. A winch lowers Campod into the water until the ocean bottom is in view by a monitor on board. Then control is transferred to an operator in the lab who uses a joystick to control the movement of Campod using the winch. The operator lowers Campod to the bottom and takes the first still shot. Then Campod is raised and re-lowered to the bottom at different location. The lateral change depends solely on the movement of the ship as the on-board operator can only control the vertical movement. Campod is lowered five times and each time it hits the bottom, a still shot is taken. The focus on Campod can be changed to zoom for up-close shots. Campod can also take a single water sample called a slurp sample. This sampling technique will 'slurp' the suspended materials near bottom in addition to the water. The sample is taken on a very gentle landing, as this minimizes the re-suspension of material.

June 16

Once the Northwest transect station was completed, a series of video-grabs was performed. Video-grab is put into the water in a similar manner to Campod. There is a camera on the equipment and when the bottom is in view an operator on board takes over the controls. The legs of video-grab land on the ocean floor and then a large barrel like structure is lowered between them to the bottom. This barrel-like structure collects a bottom sample by opening and closing around the ocean floor. The sample is brought on board where a sub-sample is taken of the sediment. Then, the sample is placed in a series of two washing grids. The sample is hosed down until all sediment is washed back into the sea. All materials that remain on the grid (shells, fish, rocks etc.) are collected, stored and brought back to shore. All species in the sample are then identified and recorded. Three full duplicate samples are collected by video-grab for each grab station. The

analysis will show the biological diversity and conditions on the ocean floor. Figure A-11 shows video-grab, and Figure A-12 shows the deck work for the event.

Figure A-11: Video-grab

Figure A-12: Washing Down Video-Grab Samples

June 17

As part of a benthic study, several moorings were deployed that contained combinations of sea scallops, Icelandic scallops and mussels. There were two types of moorings. The first type was called a HABITRAP. HABITRAPs are inverted conical structures that collect the filtered water and feces from the shellfish. The shellfish are placed along the top of the structure on netting and the water and feces fall through the cone to its vertex. The HABITRAPs will be left in the water until early fall 2000. Once the HABITRAPs

Figure A-13: HABITRAP

are retrieved, the collected material will be studied to determine contaminants that have passed through the shellfish. In addition, the rate of feces production gives clues as to the growth rate. Six HABITRAPs were deployed around the Hibernia platform. A HABITRAP is shown in Figure A-13.

The second type of mooring was called a Harp. A Harp is a Y-shaped piece of equipment that holds the three types of shellfish described above. Six Harps were placed in the water where they will be left until early fall. When the Harps are retrieved the shellfish will be shucked, and analyzed for contaminants as well as for their reproductive rates. Figure A-14, below, shows a Harps. Although, there are no pictures of Campod, it is interesting to point out that Campod is in the background (upper right hand corner) of Figure A-14.

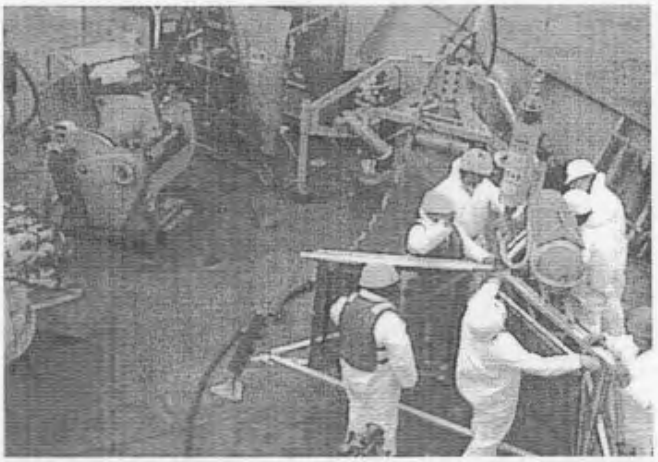


Figure A-14: Harps

For each event on the ship, data was recorded by hand, using a paper log as well as two navigation programs. A 'fix' was taken each time a piece of equipment reached its lowest depth, usually near or on the bottom. The term 'fix' means that the computer navigation systems record the time for the event.

Once the benthic moorings were released, the transect stations continued. Campod, CABLE and CTD were performed at each transect station.

June 18

The first of three anchor stations started at 10:30 AM. There were three anchor stations in total. The ship remained at each anchor station for 24 hours plus one series. A series of five events was repeated every two hours for the entire period. Each series consisted of Campod, BOB, CTD, CABLE and BOSS. There were thirteen series in total.

BOSS is the Benthic Organic Sestonite Sampler and is shown in Figure A-15. It is similar to BOB in that it collects water samples from various depths near the bottom. BOSS gives a finer view than BOB. The samples collected from BOSS were filtered and analyzed. BOSS gives a good picture of the settling rates near bottom. In addition, it shows the sediment composition at varying depths. The other four events have been described previously.

Figure A-15: BOSS

June 19

Once the first anchor station was completed at 11:00 AM, moorings were picked up. The first mooring to be retrieved was Mini-MIMS, shown below in Figure A-16. Mini-MIMS is similar to MIMS except that it is smaller and does not contain as many scientific devices as MIMS. The main device on Mini-MIMS is a current meter.

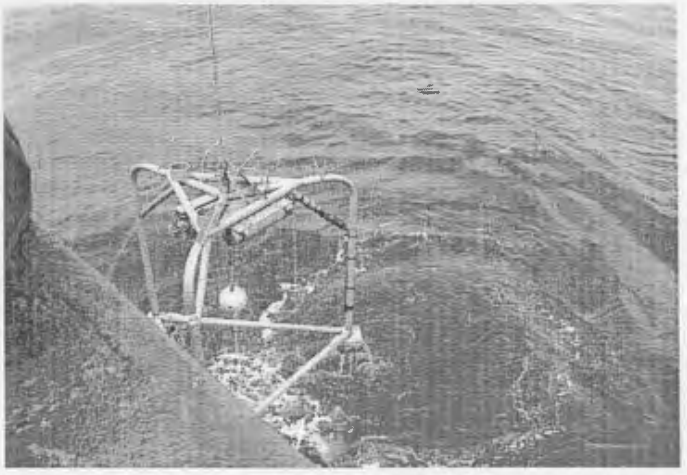


Figure A-16: Mini-MIMS

The second mooring to be retrieved was a long rope with a series of devices including a temperature gauge and a current meter. The second was called the Loder current metre. Both moorings were in place since the 1999 Hibernia expedition.

The moorings were retrieved using an acoustic release float mechanism. From on-ship, the releases were activated once the ship was near the mooring location and the floats

surfaced. The floats were still attached to the mooring below the surface. The floats were then found visually and grabbed using large hooks. The floats were brought on board and then the ropes were attached to a winch and raised until the entire mooring was securely on board.

Once both moorings were securely on board, the transect stations continued. Then the second anchor station was started at 22:30. The same series of events that was performed in the first anchor station was performed in the second.

June 20

The second anchor station continued until 23:45 when it was complete and all thirteen series of events were complete. Once the anchor station was complete, the transect stations continued. One of the stations (East - 20km) was in deeper water than the other stations. The average depth around Hibernia was about 80 m. The East -20 km transect station was about 104 m. The view of the ocean floor from Campod was much different than in the shallower water. There were several corals and more shellfish in the deeper water.

June 21

MIMS, which was put into the ocean earlier on the cruise, was collected in the morning. Once it was on board, some of the scientists downloaded the information that was collected on MIMS. Later in the day MIMS was re-deployed where it will remain until early fall 2000.

After MIMS was recovered, grappling was performed to try to recover lost moorings from the previous year. This procedure was not successful, as the proper equipment was not on board.

One lost mooring was recovered. The moorings retrieved up to this point used an acoustic release. The other type of float release is a timed mechanism. The floats are on a timer and are released on a certain date. The timing mechanism on one of the Harps

from 1999 did not work when it was to be recovered. However, before grappling was attempted on the Harp, it was noticed that the floats were present. Somehow, the floats got released from the Harp later in the year. The mooring was recovered and it was determined that most of the shellfish were still alive. These shellfish were shucked and separated into various labeled jars for testing upon return to BIO. The information gathered is expected to be quite useful as the mooring was in place for about a year.

In the afternoon, cylindrical box cores were performed to collect bottom sediment samples. The box core procedure is similar to video-grab except the sample collected is much smaller.

The last anchor station was started. Campod views later in the evening show suspected drilling muds on the ocean floor.

June 22

The last anchor station was cut to just over 12 hours. Only seven series were completed as opposed to thirteen. Each series consisted of the same five events as in previous stations. There was some problem with BOSS for awhile, and some of the samples did not get collected and therefore BOSS was eliminated for a couple of series.

The *Hudson* departed at around 15:30 to head to Sydney, NS. After this time, odds and ends were completed. The log book was checked and some of the remaining data was logged on a computer version of the log. Equipment was secured and stored.

June 23

The entire day spent steaming to Sydney. Early arrival was expected.

June 24

Arrived in Sydney, NS at 06:30. The day was spent in port. Scientists on board tried to continue repairing the broken Towcam.

June 25

The morning was spent in Sydney Harbor performing Towcam trials. Towcam appears to be working and will be used on the second leg of the cruise. The Hudson re-docked at around 13:00. The crew was changed and first crew traveled back to Halifax. The second crew went on board to start the second leg of the cruise.

APPENDIX B:
CORMIX Model Inputs and Outputs

```
CORMIX SESSION REPORT:
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
                  CORMIX: CORNELL MIXING ZONE EXPERT SYSTEM
                      CORMIX-GI Version 4.1GT
SITE NAME/LABEL:                Burrard Thermal Plant
  DESIGN CASE:                  Burrard DMS
  FILE NAME:                    C:\Program Files\CORMIX-GI\burrard.prd
Using subsystem CORMIX3:        Buoyant Surface Discharges
  Start of session:             08/16/2001--14:11:33
**************************************************************************
SUMMARY OF INPUT DATA:
--------------------------------------------------------------------------
AMBIENT PARAMETERS:
  Cross-section                         = bounded
  Width                         BS      = 1000 m
  Channel regularity            ICHREG  = 3
  Ambient flowrate              QA      = 2750 m^3/s
  Average depth                 HA      = 11 m
  Depth at discharge            HD      = 8 m
  Ambient velocity              UA      = 0.25 m/s
  Darcy-Weisbach friction factor F      = 0.03
  Wind velocity                 UW      = 2 m/s
Stratification Type             STRCND  = U
  Surface density               RHOAS   = 1020 kg/m^3
  Bottom density                RHOAB   = 1020 kg/m^3
--------------------------------------------------------------------------
DISCHARGE PARAMETERS:           Buoyant Surface Discharge
  Discharge located on                  = left bank/shoreline
  Discharge configuration               = protruding discharge
  Distance from bank to outlet  DISTB   = 35 m
  Discharge angle               SIGMA   = 90 deg
  Depth near discharge outlet   HD0     = 7 m
  Bottom slope at discharge     SLOPE   = 30 deg
  Circular pipe diameter                = 2.5 m
    Equivalent rectangular discharge:
    Discharge cross-section area A0     = 4.908739 m^2
    Discharge channel width     B0      = 1.308997 m
    Discharge channel depth     H0      = 3.75 m
    Discharge aspect ratio      AR      = 2.864789
  Discharge flowrate            Q0      = 10.000000 m^3/s
  Discharge velocity            U0      = 2.04 m/s
  Discharge density             RHO0    = 1020 kg/m^3
  Density difference            DRHO    = 0 kg/m^3
  Buoyant acceleration          GP0     = 0 m/s^2
  Discharge concentration       C0      = 100 %
  Surface heat exchange coeff.  KS      = 0 m/s
  Coefficient of decay          KD      = 0 /s
---- --------- ----------------------------------------------------------
DISCHARGE/ENVIRONMENT LENGTH SCALES:
  LQ  = 2.22 m        Lm  = 18.05 m        Lbb = 0 m
  LM  = 99999 m
--------------------------------------------------------------------------
NON-DIMENSIONAL PARAMETERS:
  Densimetric Froude number     FR0     = 99999 (based on LQ)
  Channel densimetric Froude no. FRCH   = 99999 (based on H0)
  Velocity ratio                R       = 8.15
--------------------------------------------------------------------------
MIXING ZONE / TOXIC DILUTION ZONE / AREA OF INTEREST PARAMETERS:
  Toxic discharge                       = no
  Water quality standard specified      = no
  Regulatory mixing zone                = no
  Region of interest                    = 15000 m downstream
**************************************************************************
HYDRODYNAMIC CLASSIFICATION:
  *-------------------------*
  | FLOW CLASS   = SA1 |
  *-------------------------*
**************************************************************************
MIXING ZONE EVALUATION (hydrodynamic and regulatory summary):

--------------------------------------------------------------------------
X-Y-Z Coordinate system:
Origin is located at water surface and at centerline of discharge channel:
    35 m from the left bank/shore.
  Number of display steps NSTEP = 100 per module.
--------------------------------------------------------------------------
NEAR-FIELD REGION (NFR) CONDITIONS :
Note: The NFR is the zone of strong initial mixing.  It has no regulatory
  implication.  However, this information may be useful for the discharge
  designer because the mixing in the NFR is usually sensitive to the
  discharge design conditions.
  Pollutant concentration at edge of NFR = 2.4373 %
  Dilution at edge of NFR               = 41.0
  NFR Location:                    x = 519.39 m
    (centerline coordinates)       y = 4.72 m
```

2 pipes

```
                                        z = 0 m
  NFR plume dimensions:          half-width = 30.55 m
                                   thickness = 4.27 m
-------------------------------------------------------------------------------
Buoyancy assessment:
  The effluent density is equal or about about equal to the surrounding
  ambient water density at the discharge level.
  Therefore, the effluent behaves essentially as NEUTRALLY BUOYANT.
-------------------------------------------------------------------------------
Weak contact/interaction of the discharge plume with one bank/shore occurs
  within the NFR.
-------------------------------------------------------------------------------
FAR-FIELD MIXING SUMMARY:
  Plume becomes vertically fully mixed ALREADY IN NEAR-FIELD at 0 m
  downstream and continues as vertically mixed into the far-field.
-------------------------------------------------------------------------------
PLUME BANK CONTACT SUMMARY:
  Plume in bounded section contacts one bank only at 0 m downstream.
********************** TOXIC DILUTION ZONE SUMMARY **********************
No TDZ was specified for this simulation.
********************** REGULATORY MIXING ZONE SUMMARY **********************
No RMZ and no ambient water quality standard have been specified.
********************** FINAL DESIGN ADVICE AND COMMENTS **********************
REMINDER:  The user must take note that HYDRODYNAMIC MODELING by any known
  technique is NOT AN EXACT SCIENCE.
Extensive comparison with field and laboratory data has shown that the
  CORMIX predictions on dilutions and concentrations (with associated
  plume geometries) are reliable for the majority of cases and are accurate
  to within about +-50% (standard deviation).
As a further safeguard, CORMIX will not give predictions whenever it judges
  the design configuration as highly complex and uncertain for prediction.
```

CORMIX MODEL FOR SINGLE DOE

```
CORMIX SESSION REPORT:
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
                  CORMIX: CORNELL MIXING ZONE EXPERT SYSTEM
                      CORMIX-GI Version 4.1GT
SITE NAME/LABEL:                Burrard Thermal Plant
  DESIGN CASE:                  Burrard DMS
  FILE NAME:                    C:\Program Files\CORMIX-GI\burrard.prd
Using subsystem CORMIX3:        Buoyant Surface Discharges
  Start of session:             08/16/2001--14:14:03
********************************************************************************
SUMMARY OF INPUT DATA:
--------------------------------------------------------------------------------
AMBIENT PARAMETERS:
  Cross-section                          = bounded
  Width                         BS       = 1000 m
  Channel regularity            ICHREG   = 3
  Ambient flowrate              QA       = 2750 m^3/s
  Average depth                 HA       = 11 m
  Depth at discharge            HD       = 8 m
  Ambient velocity              UA       = 0.25 m/s
  Darcy-Weisbach friction factor F       = 0.03
  Wind velocity                 UW       = 2 m/s
Stratification Type             STRCND   = U
  Surface density               RHOAS    = 1020 kg/m^3
  Bottom density                RHOAB    = 1020 kg/m^3
--------------------------------------------------------------------------------
DISCHARGE PARAMETERS:           Buoyant Surface Discharge
  Discharge located on                   = left bank/shoreline
  Discharge configuration                = protruding discharge
  Distance from bank to outlet  DISTB    = 35 m
  Discharge angle               SIGMA    = 90 deg
  Depth near discharge outlet   HD0      = 7 m
  Bottom slope at discharge     SLOPE    = 30 deg
  Circular pipe diameter                 = 2.5 m
    Equivalent rectangular discharge:
    Discharge cross-section area A0      = 4.908739 m^2
    Discharge channel width     B0       = 1.308997 m
    Discharge channel depth     H0       = 3.75 m
    Discharge aspect ratio      AR       = 2.864789
  Discharge flowrate            Q0       = 5.000000 m^3/s
  Discharge velocity            U0       = 1.02 m/s
  Discharge density             RHO0     = 1020 kg/m^3
  Density difference            DRHO     = 0 kg/m^3
  Buoyant acceleration          GP0      = 0 m/s^2
  Discharge concentration       C0       = 100 %
  Surface heat exchange coeff.  KS       = 0 m/s
  Coefficient of decay          KD       = 0 /s
--------------------------------------------------------------------------------
DISCHARGE/ENVIRONMENT LENGTH SCALES:
  LQ  = 2.22 m        Lm  = 9.03 m        Lbb = 0 m
  LM  = 99999 m
--------------------------------------------------------------------------------
NON-DIMENSIONAL PARAMETERS:
  Densimetric Froude number     FR0      = 99999 (based on LQ)
  Channel densimetric Froude no. FRCH    = 99999 (based on H0)
  Velocity ratio                R        = 4.07
--------------------------------------------------------------------------------
```

MIXING ZONE / TOXIC DILUTION ZONE / AREA OF INTEREST PARAMETERS:
  Toxic discharge = no
  Water quality standard specified = no
  Regulatory mixing zone = no
  Region of interest = 15000 m downstream

****

HYDRODYNAMIC CLASSIFICATION:

```
*------------------------*
| FLOW CLASS   = SA1 |
*------------------------*
```

****

MIXING ZONE EVALUATION (hydrodynamic and regulatory summary):

X-Y-Z Coordinate system:
Origin is located at water surface and at centerline of discharge channel:
  35 m from the left bank/shore.
  Number of display steps NSTEP = 100 per module.

NEAR-FIELD REGION (NFR) CONDITIONS :
Note: The NFR is the zone of strong initial mixing. It has no regulatory implication. However, this information may be useful for the discharge designer because the mixing in the NFR is usually sensitive to the discharge design conditions.
  Pollutant concentration at edge of NFR = 2.4373 %
  Dilution at edge of NFR = 41.0
  NFR Location: x = 519.39 m
    (centerline coordinates) y = 4.72 m
    z = 0 m
  NFR plume dimensions: half-width = 30.55 m
    thickness = 4.27 m

Buoyancy assessment:
  The effluent density is equal or about about equal to the surrounding ambient water density at the discharge level.
  Therefore, the effluent behaves essentially as NEUTRALLY BUOYANT.

Weak contact/interaction of the discharge plume with one bank/shore occurs within the NFR.

FAR-FIELD MIXING SUMMARY:
  Plume becomes vertically fully mixed ALREADY IN NEAR-FIELD at 0 m downstream and continues as vertically mixed into the far-field.

PLUME BANK CONTACT SUMMARY:
  Plume in bounded section contacts one bank only at 0 m downstream.

********** TOXIC DILUTION ZONE SUMMARY **********

No TDZ was specified for this simulation.

********** REGULATORY MIXING ZONE SUMMARY **********

No RMZ and no ambient water quality standard have been specified.

********** FINAL DESIGN ADVICE AND COMMENTS **********

REMINDER: The user must take note that HYDRODYNAMIC MODELING by any known technique is NOT AN EXACT SCIENCE.
Extensive comparison with field and laboratory data has shown that the CORMIX predictions on dilutions and concentrations (with associated plume geometries) are reliable for the majority of cases and are accurate to within about +-50% (standard deviation).

As a further safeguard, CORMIX will not give predictions whenever it judges the design configuration as highly complex and uncertain for prediction.

CORMIX MODEL FOR 4 PIPES

```
CORMIX3 PREDICTION FILE:
3333333333333333333333333333333333333333333333333333333333333333333333333333333333333333
                    CORNELL MIXING ZONE EXPERT SYSTEM
Subsystem CORMIX3:                                          Subsystem version:
 Buoyant Surface Discharges                  CORMIX-GI Version 4.1GT
------------------------------------------------------------------------------
------------------------------------------------------------------------------
CASE DESCRIPTION
 Site name/label:   Burrard Thermal Plant
 Design case:       Burrard DMS
 FILE NAME:         C:\Program Files\CORMIX-GI\burrard.prd
 Time stamp:        Mon Aug  6 11:25:28 2001

ENVIRONMENT PARAMETERS (metric units)
 Bounded section
 BS    =   1000.00  AS    =  11000.00  QA    =   2750.00  ICHREG= 3
 HA    =     11.00  HD    =      8.00
 UA    =     0.250  F     =      0.030 USTAR =0.1531E-01
 UW    =     2.000  UWSTAR=0.2198E-02
 Uniform density environment
 STRCND=  U         RHOAM = 1020.0000

DISCHARGE PARAMETERS (metric units)
 BANK  =  LEFT      DISTB =     35.00  Configuration: protruding_discharge
 SIGMA =     90.00  HD0   =      7.00  SLOPE =     30.00
 Circular discharge pipe:
 D0    =     2.500  A0    =      4.909
 Dimensions of equivalent rectangular discharge:
 B0    =     1.309  H0    =      3.750 A0    =0.4909E+01  AR    =      2.865
 U0    =     3.871  Q0    =     19.000       =0.1900E+02
 RHO0  = 1020.0000  DRHO0 =0.0000E+00  GP0   =0.0000E+00
 C0    = 0.1000E+03 CUNITS=  %
 IPOLL =  1         KS    =0.0000E+00  KD    =0.0000E+00

FLUX VARIABLES (metric units)
 Q0    =0.1900E+02  M0    =0.7354E+02  J0    =0.0000E+00
 Associated length scales (meters)
 LQ    =     2.22  LM    =  99999.00  Lm    =     34.30  Lb    =      0.00
 LQ2D  =     0.45  LM2D  =  99999.00  Lm2D  =    106.97

NON-DIMENSIONAL PARAMETERS
 FR0   =  99999.00  FRCH  =  99999.00  R     =     15.48

FLOW CLASSIFICATION
 333333333333333333333333333333333333333333
 3  Flow class (CORMIX3)      =    SA2    3
 3  Applicable layer depth HS =     8.00  3
 333333333333333333333333333333333333333333

MIXING ZONE / TOXIC DILUTION / REGION OF INTEREST PARAMETERS
 C0    = 0.1000E+03 CUNITS=  %
 NTOX  =  0
 NSTD  =  0
 REGMZ =  0
 XINT  =  15000.00  XMAX  =  15000.00

X-Y-Z COORDINATE SYSTEM:
    ORIGIN is located at the WATER SURFACE and at center of discharge
      channel/outlet:     35.00 m  from the LEFT  bank/shore.
    X-axis points downstream
    Y-axis points to left as seen by an observer looking downstream
    Z-axis points vertically upward (in CORMIX3, all values Z = 0.00)
NSTEP =100 display intervals per module
------------------------------------------------------------------------------
------------------------------------------------------------------------------
BEGIN MOD301: DISCHARGE MODULE

 Efflux conditions:
       X        Y        Z        S        C        BV       BH
    0.00     0.00     0.00      1.0 0.100E+03   3.75     0.65

END OF MOD301: DISCHARGE MODULE
------------------------------------------------------------------------------
------------------------------------------------------------------------------
BEGIN MOD302: ZONE OF FLOW ESTABLISHMENT

  Control volume inflow:
       X        Y        Z        S        C        BV       BH
    0.00     0.00     0.00      1.0 0.100E+03   3.75     0.65

 Profile definitions:
   BV = Gaussian 1/e (37%) vertical thickness
   BH = Gaussian 1/e (37%) horizontal half-width, normal to trajectory
   S = hydrodynamic centerline dilution
   C = centerline concentration (includes reaction effects, if any)
```

Control volume outflow: SIGMA = 88.47

X	Y	Z	S	C	BV	BH
0.25	-9.26	0.00	1.0	0.100E+03	4.14	1.51

Cumulative travel time = 2. sec

END OF MOD302: ZONE OF FLOW ESTABLISHMENT

BEGIN CORSURF (MOD310): BUOYANT SURFACE JET - NEAR-FIELD

Surface jet in shallow crossflow with shoreline-attachment.

Profile definitions:
BV = Gaussian 1/e (37%) vertical thickness
BH = Gaussian 1/e (37%) horizontal half-width, normal to trajectory
S = hydrodynamic centerline dilution
C = centerline concentration (includes reaction effects, if any)

X	Y	Z	S	C	BV	BH
0.25	-9.26	0.00	1.0	0.100E+03	4.14	1.51
1.78	-21.18	0.00	2.0	0.504E+02	6.67	2.58
4.06	-30.91	0.00	2.8	0.362E+02	8.11	3.97
7.68	-40.22	0.00	3.7	0.268E+02	9.86	5.55
12.67	-48.88	0.00	4.9	0.203E+02	11.87	7.33
18.90	-56.68	0.00	6.4	0.157E+02	13.98	9.23
24.27	-61.92	0.00	7.5	0.132E+02	15.54	10.67
32.12	-68.10	0.00	9.2	0.108E+02	17.48	12.51
40.57	-73.45	0.00	10.9	0.915E+01	19.22	14.22
49.41	-78.11	0.00	12.6	0.794E+01	20.75	15.78
58.54	-82.20	0.00	14.2	0.704E+01	22.10	17.19
65.51	-84.95	0.00	15.4	0.651E+01	23.01	18.16
74.95	-88.26	0.00	16.8	0.594E+01	24.10	19.35
84.50	-91.22	0.00	18.2	0.549E+01	25.07	20.43
94.14	-93.88	0.00	19.5	0.512E+01	25.94	21.42
103.84	-96.29	0.00	20.8	0.481E+01	26.74	22.32
111.16	-97.95	0.00	21.7	0.461E+01	27.28	22.96
120.95	-99.99	0.00	22.8	0.438E+01	27.96	23.74
130.77	-101.84	0.00	23.9	0.418E+01	28.57	24.47
140.63	-103.53	0.00	24.9	0.401E+01	29.14	25.14
150.51	-105.07	0.00	25.9	0.387E+01	29.66	25.76
160.41	-106.48	0.00	26.8	0.373E+01	30.14	26.34
167.85	-107.45	0.00	27.4	0.365E+01	30.47	26.75
177.78	-108.63	0.00	28.2	0.354E+01	30.89	27.26
187.72	-109.70	0.00	29.0	0.345E+01	31.27	27.73
197.67	-110.67	0.00	29.7	0.337E+01	31.62	28.17
207.64	-111.53	0.00	30.4	0.329E+01	31.94	28.58
215.11	-112.11	0.00	30.9	0.324E+01	32.17	28.87
225.09	-112.81	0.00	31.4	0.318E+01	32.44	29.22
235.07	-113.41	0.00	32.0	0.313E+01	32.69	29.55
245.06	-113.93	0.00	32.5	0.308E+01	32.92	29.85
255.05	-114.36	0.00	33.0	0.303E+01	33.13	30.13
262.54	-114.63	0.00	33.3	0.301E+01	33.27	30.32
272.54	-114.91	0.00	33.7	0.297E+01	33.43	30.56
282.54	-115.12	0.00	34.0	0.294E+01	33.58	30.77
292.54	-115.24	0.00	34.3	0.291E+01	33.70	30.96
302.54	-115.29	0.00	34.6	0.289E+01	33.81	31.13
Maximum lateral extent of recirculation bubble.						
310.04	-115.27	0.00	34.8	0.288E+01	33.88	31.24
320.04	-115.18	0.00	35.1	0.285E+01	34.00	31.42
330.03	-115.02	0.00	35.4	0.283E+01	34.13	31.61
340.03	-114.77	0.00	35.8	0.280E+01	34.29	31.82
350.03	-114.45	0.00	36.2	0.277E+01	34.47	32.04
360.02	-114.06	0.00	36.6	0.273E+01	34.67	32.28
367.51	-113.72	0.00	37.0	0.271E+01	34.83	32.47
377.50	-113.20	0.00	37.5	0.267E+01	35.07	32.74
387.48	-112.60	0.00	38.0	0.263E+01	35.32	33.02
397.46	-111.94	0.00	38.6	0.259E+01	35.59	33.32
407.43	-111.21	0.00	39.2	0.255E+01	35.87	33.64
414.91	-110.62	0.00	39.7	0.252E+01	36.10	33.88
424.87	-109.77	0.00	40.4	0.248E+01	36.41	34.22
434.83	-108.86	0.00	41.1	0.243E+01	36.75	34.58
444.78	-107.89	0.00	41.9	0.239E+01	37.09	34.95
454.73	-106.86	0.00	42.7	0.234E+01	37.45	35.33
462.18	-106.05	0.00	43.3	0.231E+01	37.74	35.62
472.12	-104.91	0.00	44.2	0.226E+01	38.12	36.03
482.05	-103.72	0.00	45.1	0.222E+01	38.52	36.44
491.97	-102.48	0.00	46.0	0.217E+01	38.94	36.87
501.89	-101.19	0.00	47.0	0.213E+01	39.36	37.31
509.32	-100.18	0.00	47.7	0.210E+01	39.69	37.64
519.22	-98.80	0.00	48.8	0.205E+01	40.13	38.10
529.12	-97.37	0.00	49.8	0.201E+01	40.59	38.57
539.01	-95.89	0.00	51.0	0.196E+01	41.06	39.05
548.89	-94.37	0.00	52.1	0.192E+01	41.54	39.54
558.77	-92.80	0.00	53.3	0.188E+01	42.03	40.03

```
    566.17   -91.60    0.00    54.2 0.185E+01  42.40    40.41
    576.04   -89.96    0.00    55.4 0.180E+01  42.91    40.93
    585.90   -88.28    0.00    56.7 0.176E+01  43.43    41.45
    595.75   -86.56    0.00    58.1 0.172E+01  43.95    41.98
    605.59   -84.80    0.00    59.4 0.168E+01  44.48    42.52
    612.97   -83.46    0.00    60.5 0.165E+01  44.89    42.92
    622.80   -81.64    0.00    61.9 0.162E+01  45.44    43.48
    632.63   -79.79    0.00    63.3 0.158E+01  45.99    44.04
    642.45   -77.90    0.00    64.8 0.154E+01  46.55    44.60
    652.26   -75.98    0.00    66.4 0.151E+01  47.12    45.17
    659.62   -74.51    0.00    67.5 0.148E+01  47.56    45.61
    669.42   -72.53    0.00    69.1 0.145E+01  48.14    46.19
  Jet/plume becomes VERTICALLY FULLY MIXED over the local ambient water depth.
     BV = water depth (vertically mixed)
    674.32   -71.53    0.00    69.9 0.143E+01  48.43    46.49
    679.22   -70.53    0.00    70.1 0.143E+01  47.72    46.58
    689.01   -68.48    0.00    70.3 0.142E+01  46.54    46.78
    698.79   -66.40    0.00    70.5 0.142E+01  45.34    46.97
    706.12   -64.82    0.00    70.7 0.141E+01  44.42    47.13
    715.89   -62.68    0.00    70.9 0.141E+01  43.19    47.34
    725.65   -60.51    0.00    71.2 0.141E+01  41.94    47.55
    735.40   -58.31    0.00    71.4 0.140E+01  40.67    47.78
    745.15   -56.08    0.00    71.6 0.140E+01  39.38    48.01
    754.89   -53.82    0.00    71.8 0.139E+01  38.07    48.25
    762.19   -52.11    0.00    72.0 0.139E+01  37.08    48.43
    771.92   -49.80    0.00    72.2 0.138E+01  35.75    48.69
    781.65   -47.46    0.00    72.4 0.138E+01  34.40    48.95
    791.37   -45.10    0.00    72.7 0.138E+01  33.04    49.22
    801.08   -42.71    0.00    72.9 0.137E+01  31.66    49.51
    808.36   -40.91    0.00    73.0 0.137E+01  30.62    49.73
    818.06   -38.48    0.00    73.2 0.137E+01  29.22    50.04
    827.75   -36.04    0.00    73.4 0.136E+01  27.81    50.36
    837.44   -33.57    0.00    73.6 0.136E+01  26.38    50.70
    847.13   -31.08    0.00    73.9 0.135E+01  24.95    51.06
    854.39   -29.21    0.00    74.0 0.135E+01  23.86    51.34
    864.07   -26.69    0.00    74.2 0.135E+01  22.41    51.73
    873.74   -24.16    0.00    74.4 0.134E+01  20.95    52.15
    883.41   -21.61    0.00    74.6 0.134E+01  19.47    52.60
    893.08   -19.04    0.00    74.8 0.134E+01  18.00    53.07
    900.33   -17.11    0.00    74.9 0.133E+01  16.88    53.45
 End of RECIRCULATION BUBBLE for shoreline-attached jet motion.
   Dilution in recirculation bubble =    82.4
   Corresponding concentration      =    0.121E+01
 Cumulative travel time =        2684. sec

END OF CORSURF (MOD310): BUOYANT SURFACE JET - NEAR-FIELD
--------------------------------------------------------------------------------
--------------------------------------------------------------------------------
** End of NEAR-FIELD REGION (NFR) **
--------------------------------------------------------------------------------

 The initial plume WIDTH/THICKNESS VALUE in the next far-field module will be
  CORRECTED by a factor  4.81 to conserve the mass flux in the far-field!
 The correction factor is quite large because of the small ambient velocity
   relative to the strong mixing characteristics of the discharge!
   This indicates localized RECIRCULATION REGIONS and internal hydraulic JUMPS.
 Flow appears highly UNSTEADY and prediction results are UNRELIABLE!
   SIMULATION STOPS!

 Some bank/shore interaction occurs at end of near-field.

--------------------------------------------------------------------------------
CORMIX3: Buoyant Surface Discharges                    End of Prediction File
333333333333333333333333333333333333333333333333333333333333333333333333333333
```

APPENDIX C:
Matlab Program Code

Program Name: stripnine.m

Program Description: File removed every ninth point from the original data set.

```
load feb05_day1t.txt
feb05_rows = size(feb05_day1t,1);
oldrowndx = 0;
ninendx   = 0;
while oldrowndx <= feb05_rows,
    oldrowndx = oldrowndx + 1;
    nineno    = 9*ninendx;
    newrowndx = oldrowndx-ninendx-1;
    if oldrowndx ~= (nineno + 1),
        feb05_mod1(newrowndx,:)=feb05_day1t(oldrowndx,:);
    end
    if oldrowndx == (nineno + 9),
        ninendx = ninendx + 1;
    end
end
save day1_eight feb05_mod1 -ascii -tabs
```

Program Name: savetime2.m

Program Description: File saved every 34th point. As a result, it saved the required points for analysis.

```
load day1_eight.txt
feb05_rows = size(day1_eight,1);
oldrowndx = 0;
thirtyfourndx = 0;
while oldrowndx <= feb05_rows,
    oldrowndx    = oldrowndx + 1;
    thirtyfourno = 34*thirtyfourndx;
    newrowndx    = oldrowndx - thirtyfourno + thirtyfourndx;
    if oldrowndx == (thirtyfourno +1),
        feb05_mod2(newrowndx,:)=day1_eight(oldrowndx,:);
    end
    if oldrowndx == (thirtyfourno + 34),
        thirtyfourndx = thirtyfourndx + 1;
    end
end
```

Program Name: stripsixnine.m

Program Description: This code removed the remaining extra data points over the total data set by removing every 69th point.

```
load day1_reduced
feb05_rows = size(day1_reduced,1);
oldrowndx = 0;
sixninendx   = 0;
while oldrowndx <= feb05_rows,
    oldrowndx = oldrowndx + 1;
    sixnineno    = 69*sixninendx;
    newrowndx = oldrowndx-sixninendx;
    if oldrowndx ~= sixnineno,
        feb05_mod3(newrowndx,:)=day1_reduced(oldrowndx,:);
    end
    if oldrowndx == (sixnineno + 69),
        sixninendx = sixninendx + 1;
    end
end
save day1_reduced2 feb05_mod3 -ascii -tabs
```

Program Name: MS2ARCS_Time05.m

Program Description: This code converted the mass spectrometer time stamp to real time and made it correspond to the time on the ARCS vehicle.

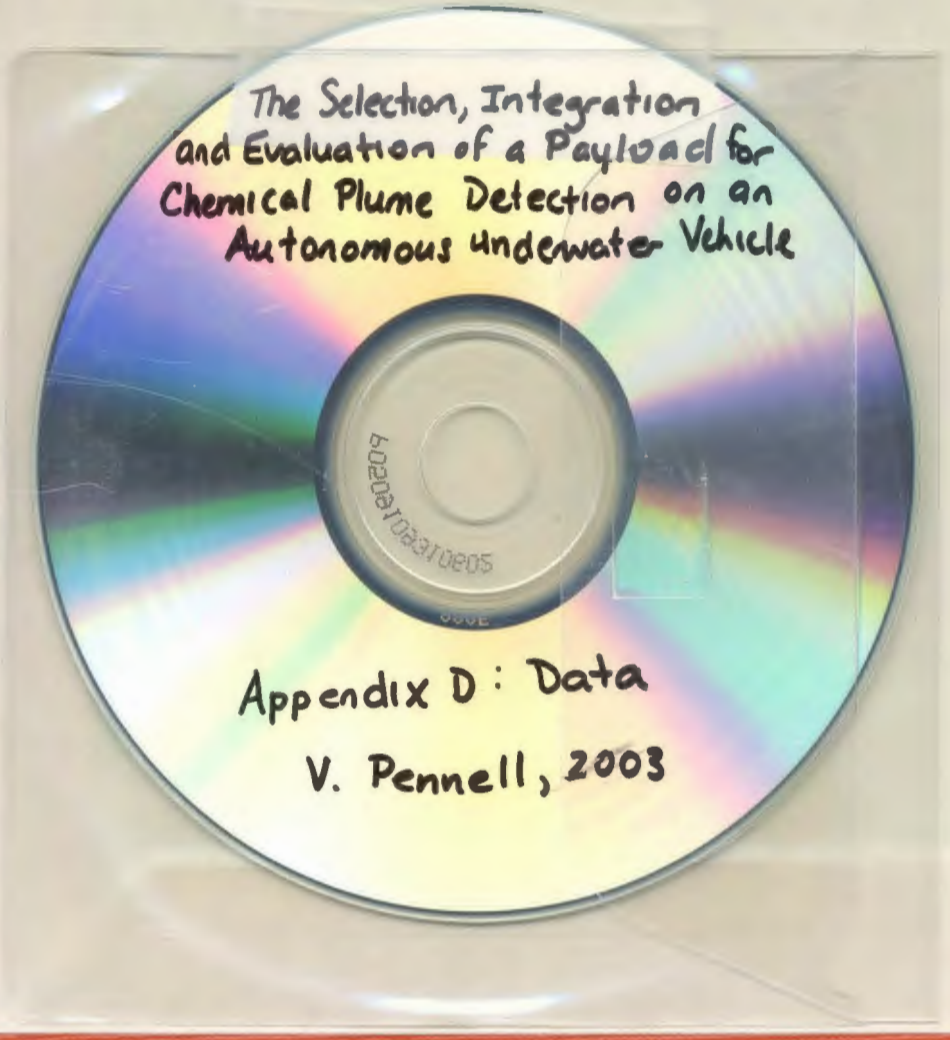
```
load MStime05.txt
MSt05_rows = size(MStime05,1);
rowndx = 0;
Min_plus = 0;
Hour_plus = 0;
while rowndx <= MSt05_rows,
    rowndx = rowndx + 1;
    ARCSTime05(rowndx,3) = MStime05(rowndx,3) + 15;
    if ARCSTime05(rowndx,3) >= 60,
        Min_plus = 1;
        ARCSTime05(rowndx,3) = ARCSTime05(rowndx,3) - 60;
    else
        Min_plus = 0;
    end
    ARCSTime05(rowndx,2) = MStime05(rowndx,2) + 17 + Min_plus;
    if ARCSTime05(rowndx,2) >= 60,
        Hour_plus = 1;
        ARCSTime05(rowndx,2) = ARCSTime05(rowndx,2) - 60;
    else
        Hour_plus = 0;
    end
    ARCSTime05(rowndx,1) = MStime05(rowndx,1) + 11 + Hour_plus;
end
save MS2ARCS_Time05 ARCSTime05 -ascii -tabs
```

Program Name: Threshold.m

Program Description: This code thresholds the data for the mass spectrometer and isolated the increasing portion of the peaks.

```
load feb05ms_run1.txt
ms47=feb05ms_run1(:,3);
ms62=feb05ms_run1(:,4);
samplenum=feb05ms_run1(:,1);

% Threshold (mutes the low-level signal, retains the higher-
level)

msthresholded = zeros(size(ms62));
threshold=3.0e-11;
idx = 1;
length = size(msproduct,1);
while idx <= length,
    if msproduct(idx) > threshold,
        msthresholded(idx) = msproduct(idx);
    else msthresholded(idx) = 0;
    end
    idx = idx + 1;
end

% To Capture the increasing portion of the DMS lobe
isIncreasing = zeros(size(msproduct));
idx = 2;
while idx <= length,
    if (msthresholded(idx) > msthresholded(idx-1)),
        isIncreasing(idx) = 1;
    end
    idx = idx + 1;
end

idx = 1;
while idx <= length,
    if isIncreasing(idx),
        msthresholded(idx) = 1;
else msthresholded(idx) = 0;
end
    idx = idx + 1;
end
```

APPENDIX D:
Mass Spectrometer Data


The Selection, Integration and Evaluation of a Payload for Chemical Plume Detection on an Autonomous Underwater Vehicle
Appendix D: Data
V. Pennell, 2003